DEPARTMENT OF COMMERCE
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George K. Burgess, Director

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By H. S. Rawdon and E. C. Groesbeck

TECHNOLOGIC PAPERS OF THE BUREAU OF STANDARDS, No. 367

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ABSTRACT

For the purpose of obtaining comparative data on the effects produced by different testing methods upon the determination of corrosion resistance of metals, tests were carried out on a copper-nickel series, consisting of copper, nickel, and three copper-nickel alloys, all of commercial grade. The testing methods tried out were simple immersion in nonaerated and aerated solutions, repeated immersion—both continuous and intermittent—spray, and an accelerated electrolytic test. The corrosive solutions, all of normal strength, employed were hydrochloric and acetic acids, sodium and ammonium hydroxides, sodium chloride and potassium dichromate (used as an oxidizing agent). A few supplementary simple immersion tests were made in which nitrogen gas replaced air for agitating the solution. The corrosion rate and the order of relative corrodibility of the five materials were found to vary very considerably for different test methods. The results clearly indicated that the essential features of the service to be met should be incorporated in any corrosion test designed to give information concerning the suitability of a metal for some particular type of service.

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I. INTRODUCTION

Much of the uncertainty concerning the relative corrosion resistances which have been reported for different metallic materials can, without doubt, be attributed to differences in the methods used in the determination of these values. The need for an impartial, comprehensive study of this subject is exemplified by a recent investigation fostered by the nonferrous corrosion committee (committee B–3) of the American Society for Testing Materials.[1] This investigation, in brief, consisted of a rather extensive series of interlaboratory corrosion tests, each laboratory using the same materials in the same solutions, the main purpose of the investigation being to show what degree of agreement may be expected in such cases when corrosion tests are made independently but in accordance with a definitely outlined procedure.

Coincident with this series of tests, in which the Bureau of Standards cooperated, there was carried out by this bureau another set of corrosion tests, the purpose of which was to show in more detail than was possible in the first series to what extent the apparent corrodibility of a metal depends upon the method of the corrosion test used. For these tests a series of metals and alloys of related composition was used in preference to a number of unrelated metals. The method was similar to that outlined by committee B–3. The results reported here are primarily for showing how the corrosion resistance of a metal is influenced by the testing method used rather than for illustrating any approved method of corrosion-resistance testing. The results of the tests, however, have warranted certain general conclusions which should be taken into consideration in any proposed scheme for determining the corrosion resistance of metallic materials.

II. TEST METHODS AND APPARATUS

1. METHODS

It is well established by the work of previous investigators that the principal controlling factors which determine the degree of corrosion of metals under any given set of conditions are, in addition to the uniformity in concentration of the corrosive solution and uniformity within the metal specimens, the degree of aeration of the solution and the opportunity for the formation, from the corrosion product as it forms, of a protective film on the surface of the metal. The various corrosion-test methods used in the series of tests summarized here permitted rather wide variations in the latter two factors.

The methods used for the series of the five metals in each of the six solutions included the following, of which the first three have found, to some extent at least, practical application in corrosion-resistance testing: (1) Complete immersion in (*a*) a still solution and (*b*) an agitated (aerated) solution; (2) repeated immersion (*a*) with and (*b*) without interruption in the cycle consisting of the immersion of the specimen and its withdrawal from the solution into the air; (3) exposure in an inclosed space to the corrosive solution "atomized" by means of a stream of compressed air into a fog or mist; and (4) anodic corrosion at very low current density.

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[1] Report of Committee B-3, Corrosion of Non-Ferrous Metals and Alloys, Proc. Am. Soc. Test. Matls., **23**, pt. 1, p. 191; 1923; and **27**, pt. 1, p. 281; 1927.

Since most of these tests were carried out simultaneously with the program of tests cooperative with committee B–3 of the American Society for Testing Materials, the same general procedure was followed. This procedure for the first three methods has been described in detail in the published reports of the committee.[2] The accelerated electrolytic test used differed considerably from that followed by the committee.[3]

2. APPARATUS

The different forms of apparatus used in the four test methods listed above and already described in complete detail in previous publications [4] are shown below by means of photographs and diagrams.

For the simple immersion test the apparatus (fig. 1) consisted essentially of a covered wooden container partially filled with water, whose temperature could be maintained by means of an electric heater and thermostat close to any desired temperature (fig. 2). A temperature of 30° C ± 1° was used for the simple immersion tests; all of the other tests were made at room temperature. The bottles, each containing about 250 ml of the corrosive solution to be used and in which the specimens were suspended, were placed in the water. The level of the water was kept the same as that of the solution inside of the bottle.

The method followed was essentially that described by Calcott, Whetzel, and Whittaker [5] as the "standard static corrosion test" developed at the Jackson Laboratory of the E. I. du Pont de Nemours Co.

Two specimens were suspended vertically in each bottle, the suspension being made by means of heavy cotton thread attached to a glass hook passing through a hole at one end of the specimen. The height of the liquid in each bottle was such as to give about 2 cm (¾ inch) of liquid above and below the immersed specimen. Sixteen bottles were placed within the container at one time.

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[2] (*a*) Report of Committee B–3 on Corrosion of Non-Ferrous Metals and Alloys, Proc. Am Soc. Test. Matls., **24,** Pt. I, p. 281; 1924; and **25,** Pt. I, p. 150; 1925. (*b*) Blum, W., and Rawdon, H. S., Principles of Electrolytic Studies on Corrosion, Am. Electrochem. Soc., Preprint 48, **51**; 1927.

[3] See note 2, (*b*).

[4] (*a*) Rawdon, H. S.; Krynitsky, A. I.; and Finkeldey, W. H., "Types of apparatus used in testing the corrodibility of metals," Proc. Am. Soc. Test. Matls., **24,** Pt. II, pp. 715–734; 1924. (*b*) Rawdon, H. S., and Krynitsky, A. I., "Notes on corrosion testing by different immersion methods," Trans. Am. Electrochem. Soc., **46,** p. 359; 1924. (*c*) See reference (*b*), note 2.

[5] Calcott, W. S.; Whetzel, J. C.; and Whittaker, H. F., Monograph on Corrosion Tests and Materials of Construction for Chemical Engineering Apparatus, D. Van Nostrand Co., New York; 1923 (reprinted from Trans. Am. Inst. Chem. Engrs., **15,** Pt. I; 1923).

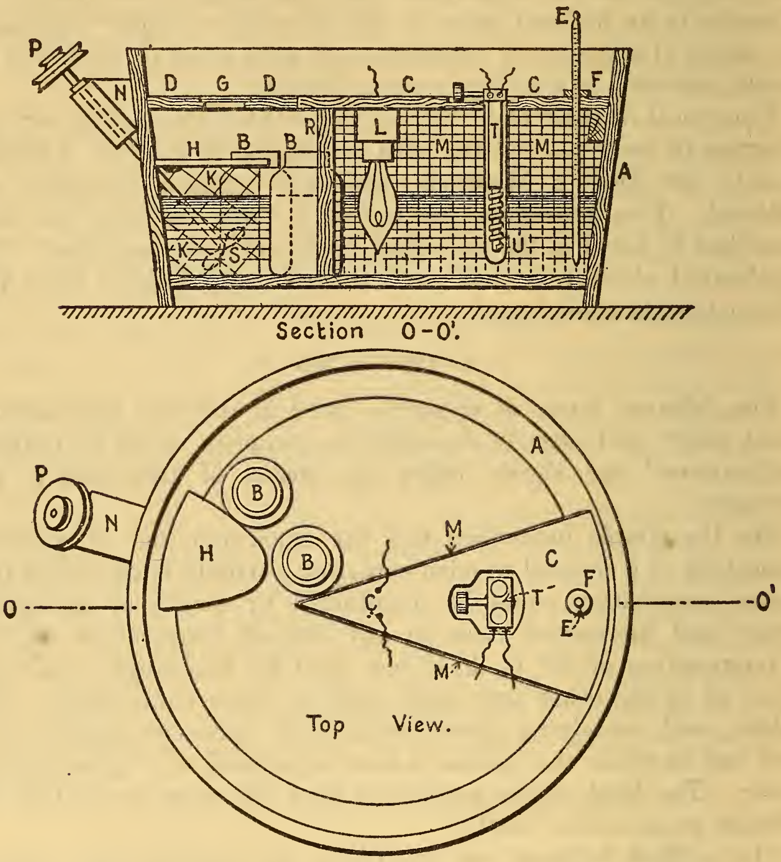

Fig. 1.—*Apparatus for conducting corrosion tests by simple immersion at constant temperature*

A, Wooden container; *B*, bottles containing corrosive solution; *C*, stationary section of wooden cover; *D*; removable section of wooden cover (not shown in top view); *E*, thermometer; *F*, cork supporting thermometer; *G*, one of two glass windows in removable cover, *D*; *H*, wooden board to protect bottles from water splashed by stirrer; *K*, 1-inch mesh wire screen attached to board *H* and surrounding stirrer; *L*, electric lamp, used as heater; *M*, one-fourth-inch mesh wire screen attached to stationary cover *C* and protecting lamp, thermostat, and thermometer; *N*, bearing and support for shaft of stirrer; *P*, pulley attached to shaft of stirrer; *R*, wooden support for narrow end of stationary cover *C*; *S*, stirrer; *T*, thermostat; *U*, glass test tube containing thermostat (and glycerine for conducting heat).

The aeration of the solution in one-half of the number of bottles was accomplished by means of a stream of compressed air which had been passed through a train consisting of a soda-lime tower for removing CO_2 and a bottle partially filled with distilled water for saturating the air with moisture and also for serving as a flow indicator. The air was delivered through a glass tube, having an inside bore of 5 mm and constricted at the tip, into the bottom of each of the bottles containing the solution and specimens. The stream of air bubbles, which was regulated to about 100 bubbles per minute, was adjusted so that the bubbles rose in the liquid between the two specimens, but not in contact with them.

In accordance with the recommendations of committee B–3, two periods of 48 hours each were used, and a fresh supply of solution was used for each period. The results of the second period were used in computing the corrosion rate. Calcott and Whetzel [6] have reported that more uniform results were obtained in the second 48-hour period than in the first. The results obtained in the present test, however, do not fully support this conclusion.

In a supplementary series of tests with two of the solutions, hydrochloric and acetic acids, nitrogen instead of air was passed through the solution in the same manner as described above.

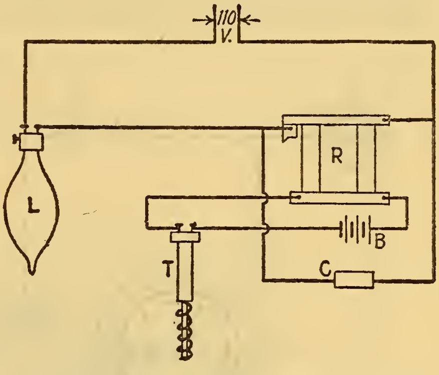

FIG. 2.—*Temperature-control arrangement used in simple immersion test apparatus (fig. 1), showing electrical connections*

L, lamp; *T*, thermostat; *R*, relay; *C*, condenser; *B*, battery

The repeated immersion tests were carried out by means of the apparatus shown in Figure 3. The essential features of this are a series of bell cranks, attached to each of which was a horizontal rod on which the specimens were suspended. As the cranks were rotated by means of a motor operating through reducing gears and a chain drive the specimens were alternately lowered into the solution and raised into the air again. In a later form of apparatus a worm drive was found much more reliable than the chain drive. In order to obtain intermittent repeated immersion, it was necessary to start and stop the motor at stated intervals (15 minutes in these tests), so that the specimen after having been immersed in the solution for approximately 1½ minutes was held in the air for the remainder of the 15-minute period, and thus was allowed to drain completely and usually to dry off before again being wetted with the solution. The timing device for accomplishing this purpose is shown in Figure 4. For the continuous repeated immersion tests in which the specimen was dipped into the solution and then withdrawn into the air, the cycle being then repeated without any interruption, no timing device was needed. A 3-minute cycle was used for the continuous repeated immersion tests.

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[6] See note 5, p. 411.

In Figure 5 (*a*) is shown the "spray box" used in carrying out the spray corrosion tests, and in Figure 5 (*b*) the device for "atomizing" the corrosive solution into the fog or mist which completely filled the chamber in which the specimens were suspended. A stream of compressed air of approximately 10 pounds pressure was employed in atomizing the solution. The outside dimensions of the box, made of Alberene stone, were about 80 cm (32 inches) by 42 cm (16½ inches) by 30 cm (12 inches) in height; the walls and bottom were 3 cm (1¼ inches) thick. A piece of plate glass served as the top cover. The specimens were suspended from glass rods, extending across inside the box, by means of glass hooks passing through a hole 0.3 cm (⅛ inch) diameter, at one end of the specimen (this detail is not shown in fig. 5 (*a*)). The 2-liter supply of corrosive solution was replaced daily during test with fresh solution.

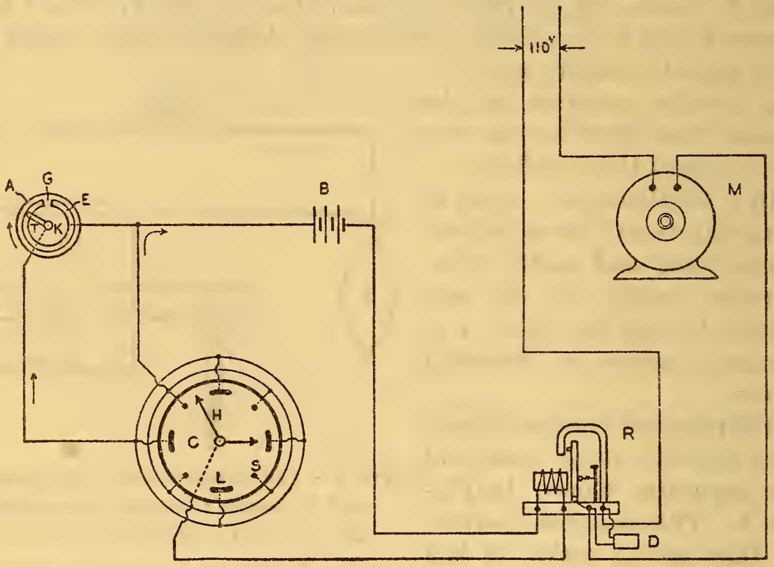

FIG. 4.—*Timing device for the intermittent repeated immersion test apparatus, showing electrical connections*

C, dial of 8-day clock; *R*, relay; *H*, minute hand with platinum contact point; *D*, 2 M. F. condenser; *L* and *S*, large and small mercury cups mounted in hard rubber ring, which is attached to *C*. Time of contact made by *H* with *L* and *S* 4 minutes and 15 seconds, respectively; *E*, metal strip mounted in bakelite disk; *G*, gap, electrically insulated; *T*, trolley fastened to end of crank shaft *K*; *K*, crank shaft of apparatus, driven by shunt wound motor *M* through worm gears

It is desirable at all times in such "spray" tests that the "drip" from the specimens be prevented from running back into the solution

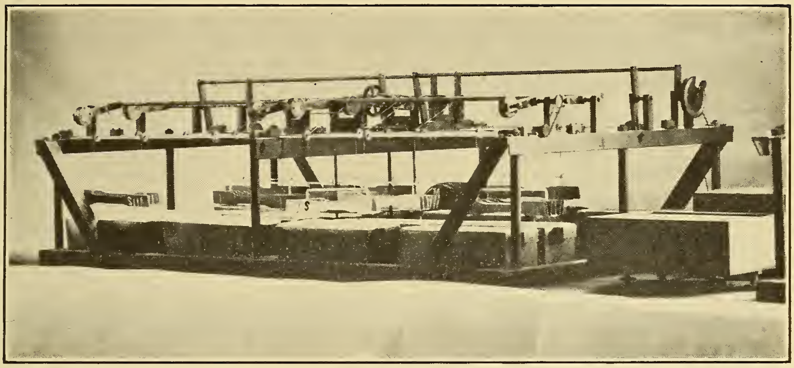

FIG. 3.—*Apparatus for conducting corrosion tests by intermittent repeated immersion*

For the continuous repeated immersion tests a similar apparatus, not provided with a timing device arrangement, was used

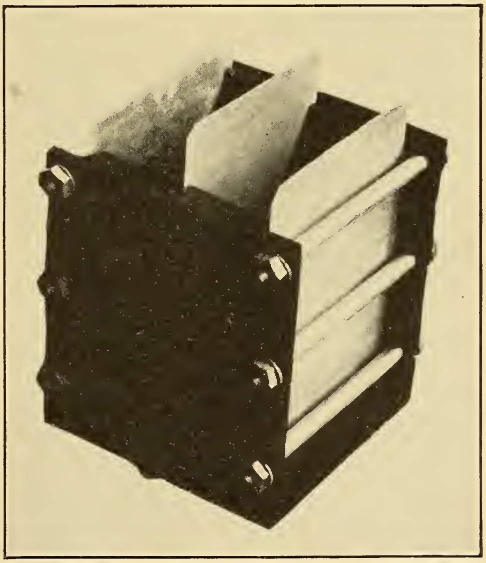

FIG. 6.—*Form of "cell" used in the accelerated electrolytic corrosion tests*

Three metal specimens of the same kind were sealed in slats in the hard rubber box, the central one being the anode; the other two, cathodes

which is to be "atomized," and this prevention is essential when specimens of different compositions are exposed at the same time to a severely corrosive solution. The transverse partition extending nearly to the top of the box was designed for this purpose. The necessity for this precaution was demonstrated early in the work when acetic acid was used for corroding a series of specimens of different kinds. The acetic acid solution was found to become contaminated with sufficient copper from the corrosion product dripping from some of the specimens, so that metallic copper was deposited on the surface of the more reactive metals, such as zinc and aluminum, from the spray formed from the contaminated solution.[7]

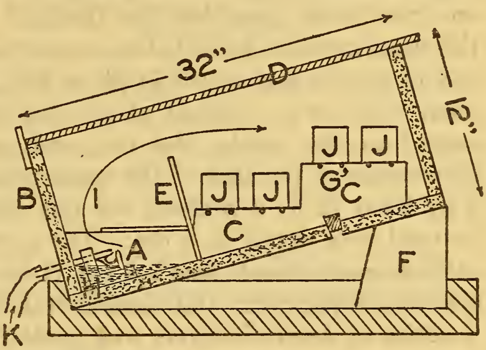

FIG. 5 (a).—*Details of spray box*

B, alberene stone box; *A*, atomizer; *H*, corrosive solution; *K*, compressed air stream; *E*, baffle plates; *I*, course of spray; *D*, glass cover; *J*, specimens; *F*, support for box

The horizontal transverse shelf in the box aided in preventing any heavy spray from reaching the specimens and also served to eliminate in very large measure swirling currents in the mist. Preliminary tests showed that, even with such precautions, it was desirable to change the position of the specimens within the box at intervals if uniform results were to be obtained. This was done daily during the test.

In the tests carried out with hydrochloric acid and ammonium hydroxide a modification of the spraying arrangement was made whereby the vertical tube of the atomizer was prolonged through a hole in the box bottom and connected by means of rubber tubing to a 6-liter Pyrex glass flask placed outside of the box and containing the corrosive solution. The waste solution inside the box was maintained at a constant level below the nipples of the atomizer, with the aid of

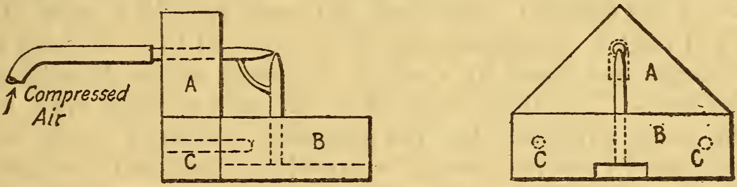

FIG. 5 (b).—*Details of atomizer used in spray box (a)*

The atomizer consists of two nipples, made from glass tubing and joined at right angles by a glass rib, and is mounted in an alberene stone frame. The corrosive solution is sucked up through the vertical nipple by the air stream

Parts *A* and *B* of the frame are fastened together with wooden plugs, *C* an inverted U-shaped siphon placed over the wall above the atomizer. In this modified arrangement the flow of corrosive solution into the box was throttled down as far as practicable and amounted to 3 to 4 liters per 24 hours.

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[7] See note 2, reference (*a*), vol. 25.

The accelerated electrolytic corrosion tests were carried out by means of the "cell" shown in Figure 6, which is a modification of the one previously described by Haring.[8] Three similar specimens of the sheet metal to be tested were inserted into slots in the hard-rubber box as shown and sealed in place with paraffin. The central specimen, which was weighed at the beginning and close of each test, served as the anode; the two end specimens as cathodes. The dimensions of the face of the specimens wetted by the solution were 5 by 5 cm (2 by 2 inches), the box being filled with the solution to be used to a depth of 5 cm. The distance between the anode and cathode on each side was 2.5 cm (1 inch). Details of the necessary electrical equipment and connections have already been published.[9] A series of determinations was made [10] with each specimen in each solution at room temperature, the current density being increased slightly for each successive "run." The current density in all cases was low and varied from 0.001 amp./dm^2 to 0.02 amp./dm^2. No attempt was made to agitate or aerate the solution.

III. MATERIALS

1. METALS

Nickel and copper, together with three nickel-copper alloys with nickel contents of approximately 29, 45, and 67 per cent, were used. The differences in the order of corrodibility shown, according to the results of the different methods of test used, by such a series of materials of related composition should be expected to be of much more significance than those by a set of unrelated metals determined in similar tests. The alloys were all of the solid solution type, hence it was to be expected that the corrosion resistance would not be complicated by the existence of a two-phase structural condition, as is often true for alloys. All of the materials were commercial products, and were used in the hot-rolled state. The compositions are summarized in Table 1.

These materials do not differ much in density, the value for copper and nickel determined at 20° C. being 8.847 g/cm^3 and 8.925 g/cm^3, respectively.[11] The densities of the three alloys are intermediate between the values for nickel and copper. Since the density values are so close to one another, it is not necessary for comparing their rates of corrosion to convert the corrosion losses, as expressed in "loss of weight per unit area," into "depth of penetration," as is the case with metals differing widely in density—as, for example, aluminum and copper.

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[8] Haring, H. E., "A simple method for measuring polarization and resistivity," Trans. Am. Electrochem. Soc., **49**, p. 417; 1926.

[9] See note 2, reference (*b*), p. 411.

[10] By W. A. Tucker, scientific aid, Bureau of Standards.

[11] Density determinations, by E. L. Peffer, physicist, Bureau of Standards.

TABLE 1.—*Composition of specimens used in the corrosion tests* [1]

Material	Element determined						
	Nickel [2]	Copper	Manganese	Iron	Tin	Carbon	Silicon
	Per cent	*Per cent*	*Per cent*	*Per cent*	*Per cent*	*Per cent*	*Per cent*
Nickel	98.8	0.19	0.17	0.62	---------	0.10	0.03
Alloy No. 1 (Monel metal)	70.1	27.8	.33	1.65	(3)	.10	.01
Alloy No. 2 (cupro nickel)	44.6	53.9	1.0	.35	(3)	.10	.02
Alloy No. 3 (Admiralty nickel)	28.9	69.7	.10	.25	1.0	.07	.01
Copper	---------	99.9	---------	.01	---------	---------	---------

[1] The analyses were made under the direction of J. A. Scherrer, chemist, Bureau of Standards.

[2] No separate determination was made of the cobalt content, which amounts, presumably, to 0.5 to 1.0 per cent for nickel metal and to proportionally smaller percentages for the nickel-copper alloys.

[3] Not detected.

2. SOLUTIONS

The solutions used for corroding the metals were those used in the program of committee B–3.[12] They were as follows: Hydrochloric acid, acetic acid, sodium hydroxide, ammonium hydroxide, sodium chloride, and potassium dichromate. A normal solution was used in each case, the dichromate solution being made normal with respect to its oxidation value and not to its hydrogen equivalent.

Preliminary corrosion tests made with solutions of the acids before and after distillation indicated that no useful purpose would be served by a preliminary purification of these materials such as had been recommended.[13] The difference in the average results obtained with solutions of the distilled and of the undistilled acids was negligible, being no greater than the variations encountered in any "run" of four specimens corroded under the same conditions. The results show that high-grade stock materials of c. p. quality should be entirely satisfactory for corrosion tests of the kind discussed here.

3. PREPARATION OF SPECIMENS

All of the materials were in sheet form and, with the exception of alloy No. 3, were 0.25 cm (1/10 inch) thick. The latter was only one-fifth of this thickness. For all the tests, excepting the accelerated electrolytic corrosion test (see Section II, 2, p. 411, and also note 2, reference (*b*), p. 411, for method of preparing specimens for test), rectangular specimens 2.5 by 5 cm (1 by 2 inches), were machined from the sheets. The surface area of such a specimen is 28.75 cm^2 for the thicker material and 25.75 cm^2 for the thinner sheet (alloy

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[12] See note 2, reference (*a*) vol. 24.

[13] See note 12.

No. 3). In every case, however, the dimensions of each specimen were measured and the area corresponding to the measured dimensions used in computing the corrosion loss per unit of area instead of using the average surface area.

The surface of the specimens was cleaned by being rubbed with a piece of emery paper 1G by means of the finger. This was followed by Hubert emery paper 0 and 00 grades, applied in the same manner. By this means surface imperfections, such as scratches and shallow indentations, were easily and quickly removed, thus leaving a comparatively smooth, though not always truly flat, surface. In each case the paper was rubbed so that the scratches formed would be at right angles to those already on the surface of the specimen. When placed in position for testing, the specimens were suspended so that the scratches left by the final polishing were vertical. A series of earlier tests had shown that grinding the surfaces flat by the methods commonly used in metallography was not only very laborious, but unnecessary in that it led to a no higher degree of accuracy in the results obtained upon corrosion.

Each specimen was weighed before being corroded. Before weighing, the surface was rubbed with alcohol, rinsed with ether, and the specimen allowed to stand in a desiccator for at least one-half hour. In all cases, the rule of starting the corrosion test within 24 hours after the specimens had been weighed was followed. Four specimens of each kind were used in each test made in the various corroding media under the different testing conditions.

The specimens were, at the conclusion of the test period in the repeated immersion test and of each periodic run in the simple immersion and spray tests, brushed with a stiff bristle brush to remove any adhering deposits of corrosion products, then washed in water, rubbed with alcohol, and rinsed in ether. The copper specimens were the only ones to offer any difficulty in the removal of corrosion products adhering to the surface of the specimen, especially those tested by the spray method in hydrochloride acid, sodium and ammonium hydroxides and those tested by the simple immersion and repeated immersion methods in sodium and ammonium hydroxides. With the hope of loosening the firmly adhering deposit, these specimens were allowed to stand in very hot water for a few minutes, followed by vigorous brushing, but without much avail. However, these specimens had shown a considerable loss in weight, even with the deposit adhering to them. Some months after the conclusion of these tests these specimens were immersed in a 10 per cent sulphuric acid solution for 30 seconds with the result that the deposit was quite completely removed, thus leaving the underlying metal surface quite clean, though dulled, in appearance. Some preliminary experiments made on several polished copper specimens had shown that the average total loss in weight produced by three dippings of 30 seconds each in sulphuric acid of the same strength was no greater than 0.3 mg. The data reported in this paper for the copper specimens do not take into account the additional loss of weight incurred by the removal of the deposit in the acid treatment. The additional loss of weight produced by the acid treatment was found to vary over a rather wide range, that for the specimens tested in sodium hydroxide by the repeated immersion and spray methods being large, yet the relative positions of copper in the various figures in this paper remained unchanged.

IV. CONDITIONS OF EXPOSURE IN THE VARIOUS TEST METHODS

It would be well to consider here the conditions which surround the specimens exposed in the various types of corrosion testing and the important factors likely to be met with.

1. SIMPLE IMMERSION

In the nonaerated test the solution is quiescent and is constantly absorbing oxygen from the overlying atmosphere, although the amount of oxygen absorbed is very much less than that when the air is bubbled through the solution. The rate at which the dissolved oxygen reaches the corroding metal by convection and diffusion depends on the nature and concentration of the solution, on the ratio of the surface of the solution to its volume, and to the distance intervening between the surface and the specimen. Since there is comparatively little movement in the solution, the oxygen supply in the vicinity of the specimen soon becomes impoverished because of the slow diffusion of oxygen from the outlying portions of the solution, and consequently the initial type of corrosion (electrochemical attack accelerated by the presence of oxygen) may be replaced by another type of corrosion. This later type may be due to "differential aeration" (see Section VI, 2, p. 441) set up by either the difference in concentration of oxygen in the neighborhood of the specimen and in the outlying portions of the solution ("oxygen concentration cell") or the film of corrosion products which covers part or all of the metal surface and thereby serves to screen the underlying metal from the oxygen supply in the outlying liquid. The two important factors—rate of oxygen supply and movement of corroding solution—will assume a different aspect by the aeration of the solution. Here a fresh supply of oxygen will continually be brought to the metal surface, and any film of corrosion products that may form over the metal surface would tend to be swept away by the movement of the corroding solution set up by the stream of air. The net result should be a greater degree of corrosion of the specimen because of the greater supply of oxygen furnished to the metal surface. The temperature factor is negligible in this method of corrosion testing, since the tests are run in a water bath at a constant temperature.

2. REPEATED IMMERSION

More factors are involved in testing by the repeated immersion method than is the case by the simple immersion method. While the manner in which the specimens are exposed to oxidizing conditions is the same in both the intermittent and continuous immersion test methods, the opportunity for absorption of oxygen by the corrosive solution adhering to the specimens, and consequently the degree of corrosion produced, should be greater for the latter, since the specimens are kept wetted for a considerably greater period of time. (See Section VI, 2, p. 441.) By reason of the longer period of suspension in the air and the correspondingly greater opportunity for getting dry there may be formed on the surfaces of the intermittent immersion specimens, in the case of certain combinations of metal and corrosive solution, more of a protective film or a strongly adhering deposit of corrosion products. Such a condition may have an important bearing on the subsequent rate of corrosion. Other factors which may exert an influence on the test results, unless provision is made for their control, are temperature, humidity, circulation of air, presence of laboratory fumes, and, possibly, the ultra-violet rays from the sunlight, especially as the testing apparatus is not inclosed and, therefore, is exposed to surrounding conditions.

3. SPRAY

The degree of aeration in the spray test is large, hence oxygen plays an important rôle. Since any of the corrosive solution which the specimen comes in contact with must be that condensed from the "fog," one should not expect to find much more than a film of the solution spread over the specimen or drops and small pools scattered over various portions of the surface. Hence, the corroding of the specimen may not be uniform in nature and extent, as compared with that obtained in simple and repeated immersion. There are opportunities for the formation of a protective film or a deposit of corrosion products, but one would hardly expect them to be as adherent as in repeated immersion unless the test were stopped during the course of the test run and the specimens were allowed to get dry. It should be noted that the conditions obtaining in the "spray" test do not afford as great an opportunity for differential aeration to set in as in simple and repeated immersion. (See Sections IV, 1, p. 419, and VI, 2, p. 441.) As this test is an inclosed one, there would be a slower response, in the case of operation at room temperatures, to variations in the temperature of the surrounding atmosphere, and, hence, the temperature factor should be of little importance unless the temperature outside varied over a wide range. The test can be operated at any chosen, constantly maintained, temperature by means of a thermostatically controlled heating arrangement placed in the spray box or by some other suitable means. The air pressure used to atomize the corrosive solution should be kept as constant as practicable in order to insure consistent testing conditions.

4. ACCELERATED ELECTROLYTIC CORROSION

The use of any electrolytic corrosion test is based upon the assumption that, if corrosion is essentially electrolytic in character, it is reasonable to accelerate it by the application of an e. m. f. The potential used in the tests in this investigation was such as to give very low current densities, much more nearly comparable to the conditions obtaining under actual corrosion conditions than in the tests of a similar kind previously described. Of the various other tests used in the present investigation, the results of the accelerated electrolytic tests would be expected to be most comparable with those obtained by simple immersion in nonaerated solutions. The relative corrodibility of the different materials as determined by anodic corrosion may be expressed as (*a*) the different losses of weight resulting from the flow of current produced by the same potential for all of the materials or (*b*) the potentials required to produce the same loss of weight in the different materials in the same time.

V. RESULTS

In Figures 7 to 11 are summarized the results obtained with the different materials in the various solutions when corroded by the simple immersion and by repeated immersion methods. The results obtained by these two immersion methods have been included in the same figure in order to facilitate the comparison of the two. In all cases the result plotted was the average obtained for four specimens, all of which were tested at the same time and under the same conditions. The deviation from the average has been indicated also in each case by arrows. The pronounced accelerating effect of aeration in corrosion tests as ordinarily carried out is illustrated by Figure 12, in which are summarized the results obtained in simple immersion tests wherein nitrogen was used instead of air for agitation of the solution, the conditions being otherwise unchanged.

In Figures 13 to 18 are summarized results showing the progress of the spray-corrosion tests during the 30-day period. The average rates of corrosion (loss in mg/dm^2/24 hours) as determined from the longer tests are given in Figure 19.

The results of the accelerated electrolytic tests are given in Figures 20 to 25 in the form of current density : potential and loss of weight : potential curves. The theoretical losses of weight for nickel and

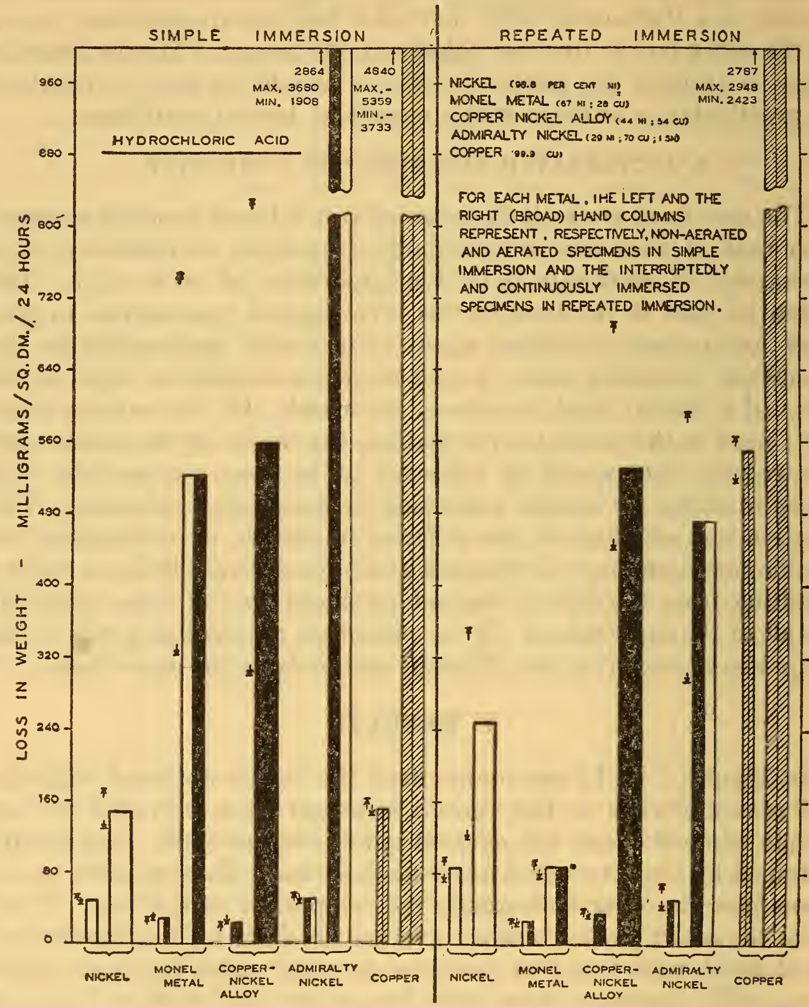


Fig. 7.—*Results of corrosion tests in N hydrochloric acid solution; simple immersion and repeated immersion methods*

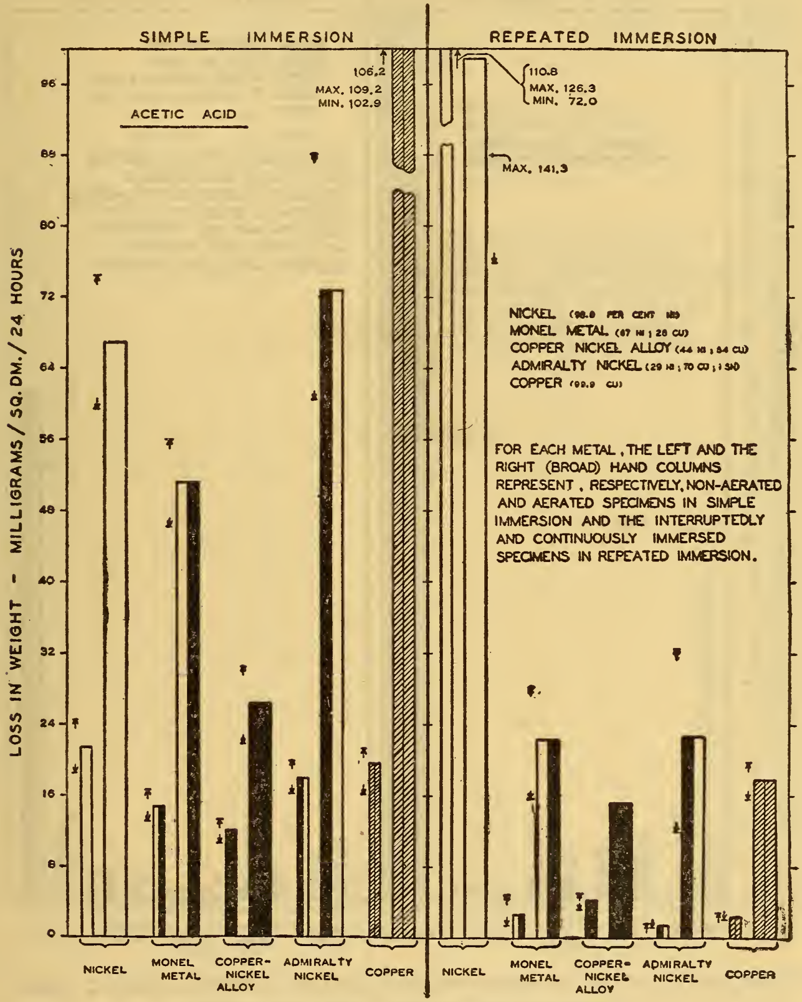
The average values reported are for four specimens, each 5 by 2.5 by 0.5 cm (the Admiralty nickel specimens were 0.05 cm thick), except in one case (indicated by an asterisk at upper right corner of column) in the repeated immersion tests where results for only three specimens were available

copper for the different current densities resulting from the three or four potentials used were calculated on the basis of Faraday's laws and have been plotted as dotted curves in the loss of weight : potential series of curves.

VI. DISCUSSION

1. RELATIVE VALUE OF DIFFERENT TESTS

The foregoing results clearly demonstrate that the corrosion resistance of a metal may be influenced very markedly by the method used in carrying out the corrosion test. An obvious conclusion from this is that any "practical" corrosion test should embody the essential features of the service for which the material is to be used. In other words, the essential features of the service conditions under



FOR EACH METAL, THE LEFT AND THE RIGHT (BROAD) HAND COLUMNS REPRESENT, RESPECTIVELY, NON-AERATED AND AERATED SPECIMENS IN SIMPLE IMMERSION AND THE INTERRUPTEDLY AND CONTINUOUSLY IMMERSED SPECIMENS IN REPEATED IMMERSION.

FIG. 8.—*Results of corrosion tests in N acetic acid solution; simple immersion and repeated immersion methods*

The average values reported are for four specimens, each 5 by 2.5 by 0.5 cm (the Admiralty nickel specimens were 0.05 cm thick) which a metal is to be used should be incorporated into a corrosion test which is designed to give information concerning the suitability of the metal for any particular type of service. Recommendations based upon the results of one type of corrosion test may at times be very misleading when applied to another type of service, as is illustrated by the resistance of the five materials to corrosion by hydrochloric acid when applied as a spray or by some of the immersion methods. Not only was the corrosion resistance of all the ma-

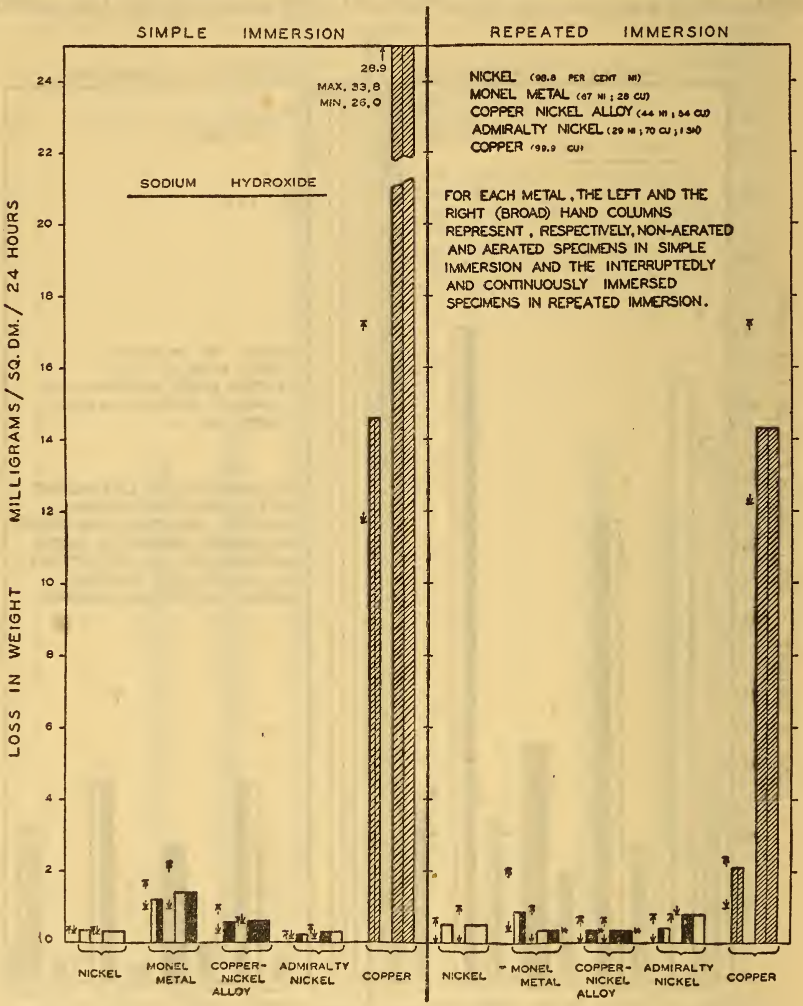


FIG. 9.—*Results of corrosion tests in N sodium hydroxide solution; simple immersion and repeated immersion methods*

The average values reported are for four specimens, each 5 by 2.5 by 0.5 cm (the Admiralty nickel specimens were 0.05 cm thick), except in three cases (indicated by an asterisk at upper right corner of column) in the repeated immersion tests where results for only three specimens were available terials very much better when determined by the spray method, but the relative order of resistance of the five was not the same as that determined by the other methods. In particular, it will be noted that copper, according to the spray test, would be rated as fairly resistant to hydrochloric acid and somewhat better than some of the alloys, whereas according to immersion methods, in which the degree of aeration was comparable to that of the spray test, copper was rated as having a resistance much lower than any of the others.

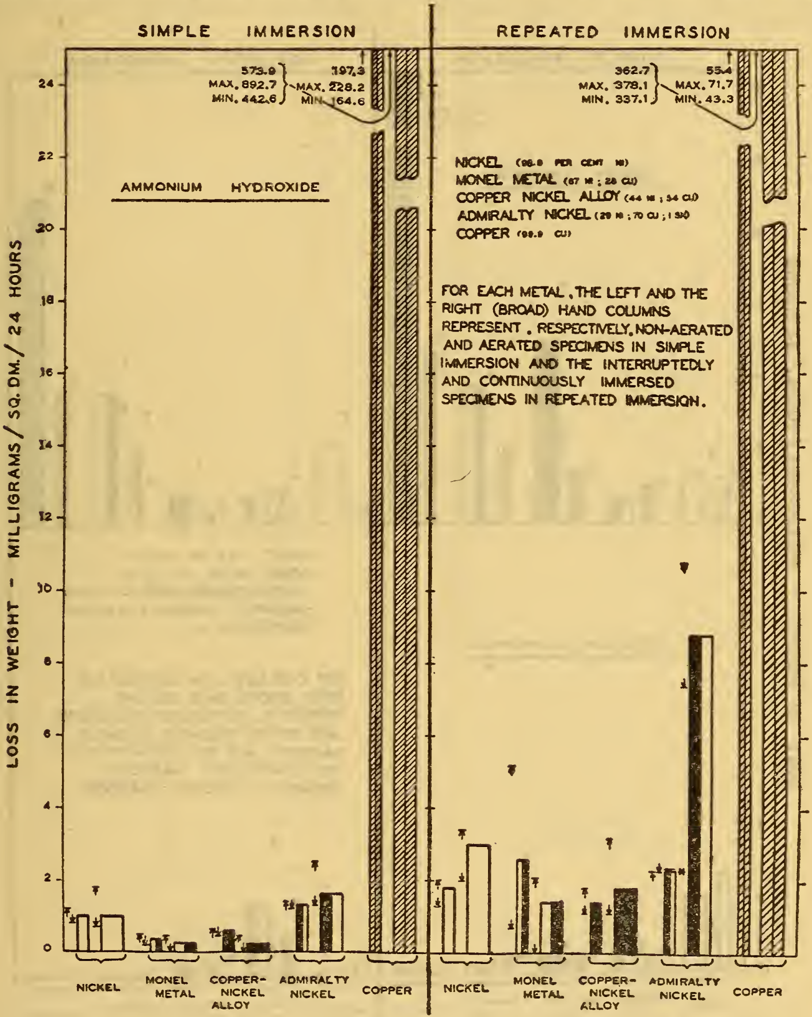


Fig. 10.—*Results of corrosion tests in N ammonium hydroxide solution; simple immersion and repeated immersion methods*

The average values reported are for four specimens, each 5 by 2.5 by 0.5 cm (the Admiralty nickel specimens were 0.05 cm thick), except in one case (indicated by an asterisk at upper right corner of column) in the repeated immersion tests where results for only three specimens were available

For any one of the various solutions the materials were rated in a somewhat different order of corrosion resistance according to the method of test used. This is best shown by the results obtained with the two acids. In the other solutions the resistance of the nickel-containing materials was often of so nearly the same magnitude that the test results could not be relied upon as a means for discriminating closely between any one metal and its companions. In Table 2 (p. 430) the materials have been placed in order of their

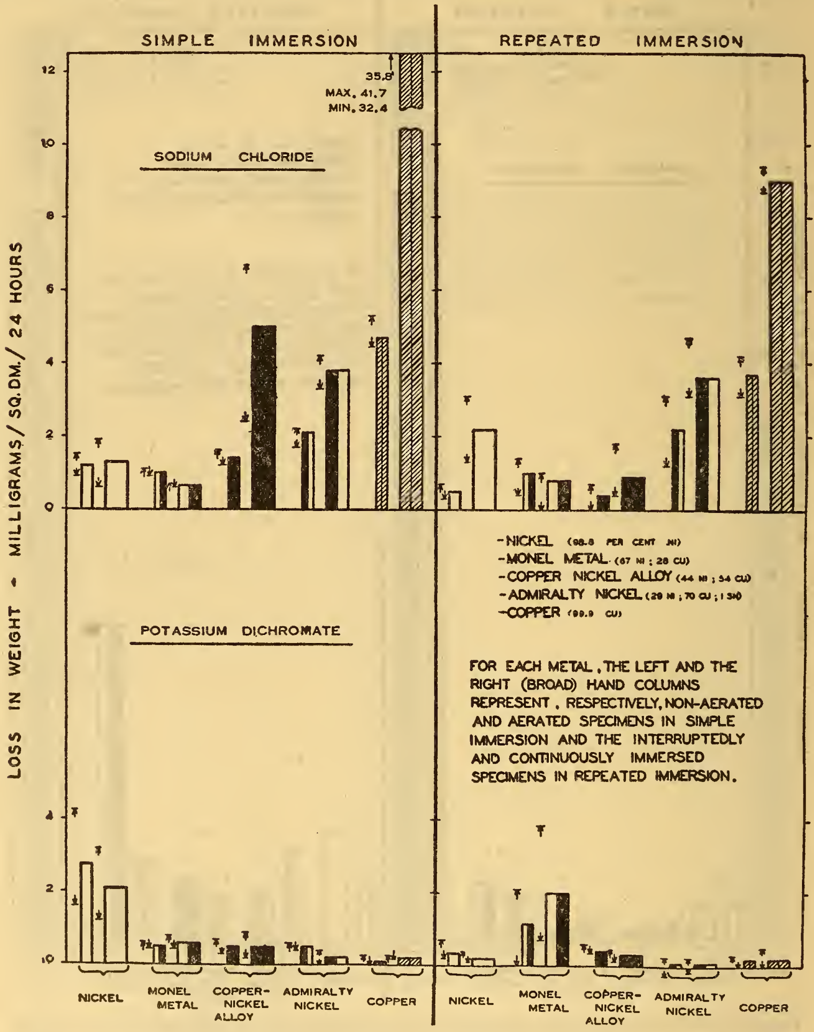


Fig. 11.—*Results of corrosion tests in N sodium chloride and potassium dichromate solutions; simple immersion and repeated immersion methods*

The average values reported are for four specimens, each 5 by 2.5 by 0.5 cm (the Admiralty nickel specimens were 0.05 cm thick) relative corrosion resistance as determined by the various test methods for the two acid solutions. The relative corrosion resistances of the materials as determined by the accelerated electrolytic method have been based upon the portions of the curves lying within the range 0 to approximately 0.10 g/dm²/24-hour loss in weight (figs. 20 (*b*) and 21 (*b*)), where the current density is low. At low

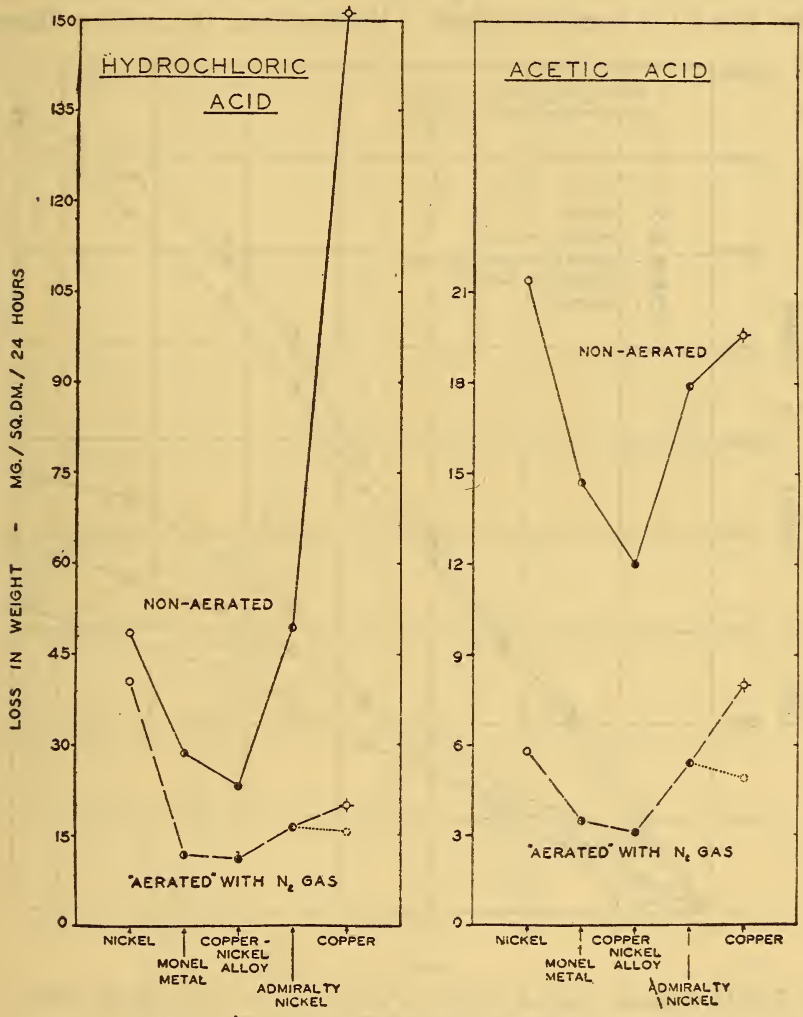


FIG. 12.—*Results of simple immersion tests in which nitrogen gas was used for "aerating" the hydrochloric acid and acetic acid solutions*

The lower (dotted circle) of the two values for copper were obtained in a special run where a quite brisk bubbling of nitrogen gas into the solution was maintained for 45 minutes before and 35 minutes after the specimens were placed in the test bottles with the object of decreasing the attack of copper by driving out as much as practicable of the dissolved oxygen from the solution and of the oxygen from the atmosphere overlying the solution in the test bottles current densities there is a greater freedom from interfering phenomena, such as passivity of the metal, presumably as a result of the formation of an invisible surface film, and the formation of visible protective films of corrosion products which would likewise tend to slow down the corrosive attack. Furthermore, the greater dispersion of the curves within this range lends itself to a more ready differentiation. It will be seen that in no two cases were the materials rated in exactly the same order of corrosion resistance. For practical purposes, of course, the differences in some cases would be of no significance. The results serve to show, however, the degree of agreement that may be expected in corrosion-resistance testing.

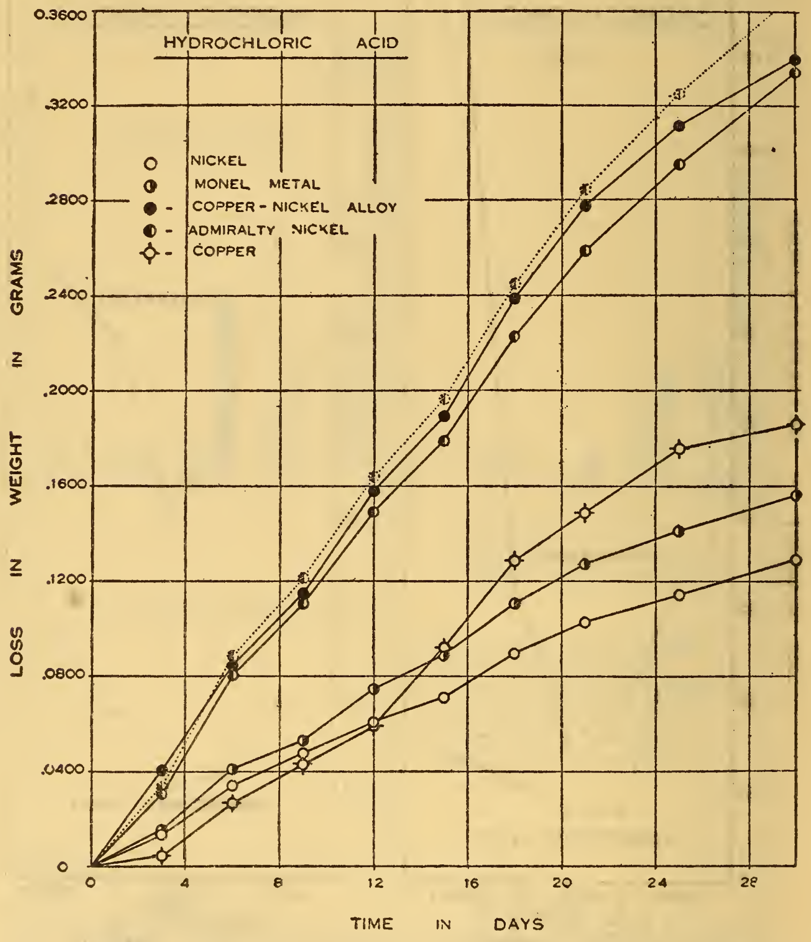


FIG. 13.—*Results showing progress of spray corrosion tests during 30-day period; N hydrochloric acid solution*

As the Admiralty nickel specimens were only one-fifth as thick as those of the other metals, there is included an additional curve (dotted) which shows the computed loss in weight for Admiralty nickel specimens of the same thickness as the other specimens (also in figs. 14 to 17, inclusive)

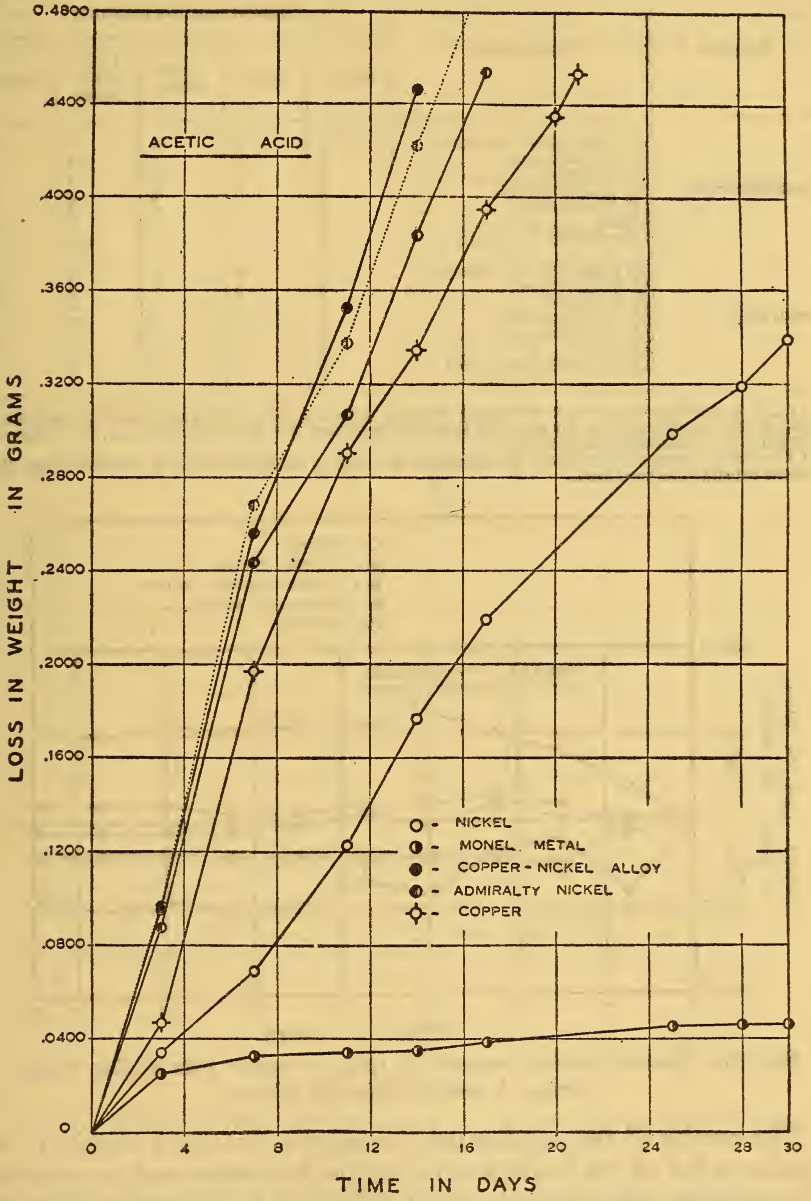


FIG. 14.—*Results showing progress of spray corrosion tests during 30-day period; N acetic acid solution*

Table 2.—*Order of corrosion resistance of the five materials in hydrochloric and acetic acid according to the test method*

Solution	Test method	Order of corrosion resistance [1]				
		Nickel	Monel	Copper nickel	Admiralty nickel	Copper
Hydrochloric acid	S. I. agitation by nitrogen	5	*2	*1	3	4
	S. I. nonaerated	*3	2	1	*4	5
	S. I. aerated	1	*2	*3	4	5
	R. I. intermittent	4	1	2	3	5
	R. I. continuous	2	1	4	3	5
	Spray	*1	*2	4	5	3
	Accelerated electrolytic [2]	*4	1, 2	3	1, 2	*5
Acetic acid	S. I. agitated by nitrogen	*4	*2	*1	*3	5
	S. I. nonaerated	5	2	1	3	4
	S. I. aerated	3	2	1	4	5
	R. I. intermittent	5	*3	*4	*1	*2
	R. I. continuous	5	*3	1	*4	2
	Spray	2	1	*5	*4	3
	Accelerated electrolytic [2]	*2	1	*4	5	*3

[1] 1, 2, 3, 4, and 5 indicate order of decreasing corrosion resistance; for any horizontal line, the asterisks (*) indicate that the difference in the corrosion rates thus indicated was only very slight. S. I.=Simple immersion. R. I.=Repeated immersion.

[2] The relative corrosion resistance corresponding to a loss of approximately 0.10 g/dm²/24 hours (low current density) has been used.

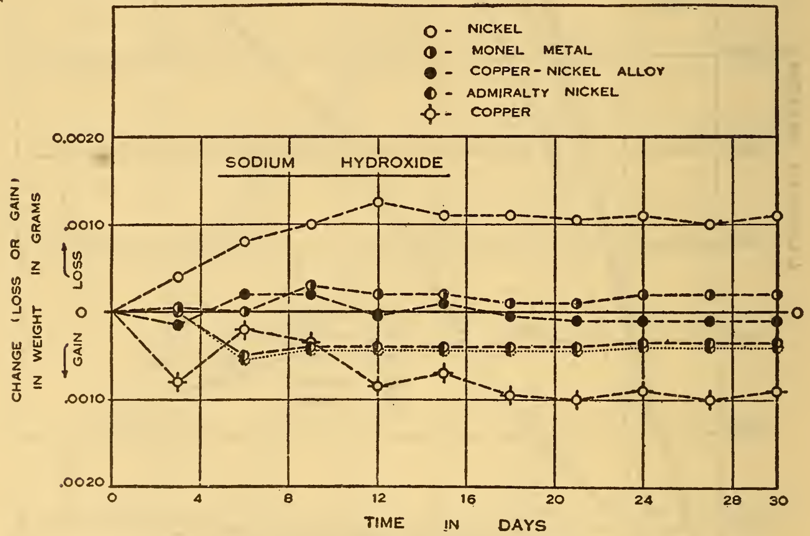


Fig. 15.—*Results showing progress of spray corrosion tests during 30-day period; N sodium hydroxide solution*

The results of the accelerated electrolytic test serve strikingly to confirm a few of the findings of the simple immersion and spray tests. For example, the relatively small difference in the corrodibility of copper and nickel in hydrochloric acid in oxygen-free solutions (fig. 12) and in the spray test (fig. 13) was also shown by the electrolytic method (fig. 20 (*b*)). The decidedly superior corrosion resistance of Monel metal against acetic acid as compared with the other two alloys (fig. 14) was also confirmed (fig. 21 (*b*)). The results obtained in the sodium and the ammonium hydroxide solutions in which the alloys of high-nickel content readily become passive were in good agreement with those of the corresponding simple immersion tests. In these solutions the results of the electrolytic corrosion test serve

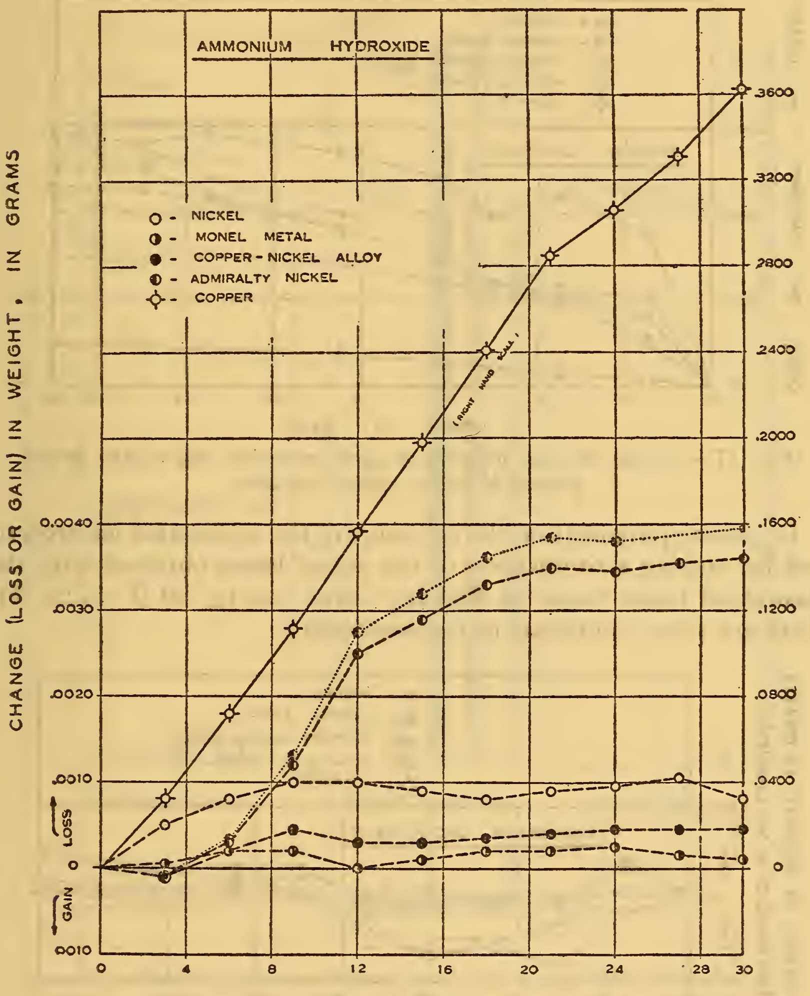


FIG. 16.—*Results showing progress of spray corrosion tests during 30-day period; N ammonium hydroxide solution*

admirably to demonstrate the widely differing corrosion resistance of the various materials. In the chloride solutions the order of corrosion resistance as determined by the electrolytic test was in fair agreement with that shown by simple immersion in unaerated solutions. In potassium dichromate, however, the order was reversed. On the whole, the agreement between the relative corrosion resistance of the metals as determined by the accelerated electrolytic test and that from the corresponding simple immersion tests in unaerated solutions was somewhat better than in those tests in which aeration was an important factor.

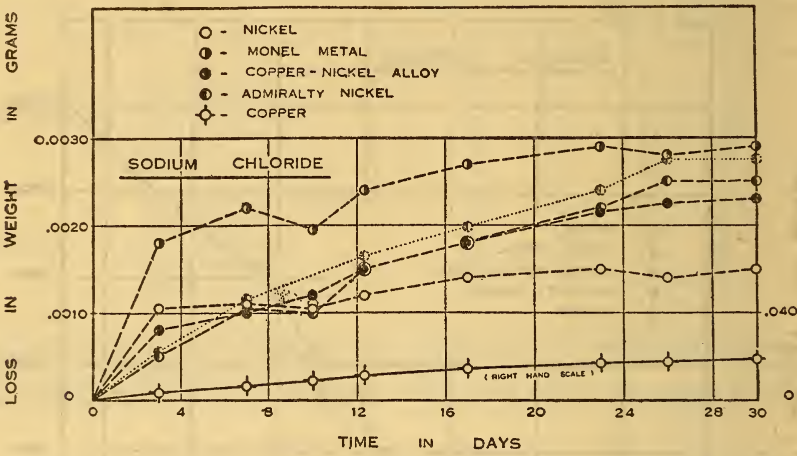


FIG. 17.—*Results showing progress of spray corrosion tests during 30-day period; N sodium chloride solution*

In passing judgment on the efficiency of the accelerated electrolytic test by making a comparison of the actual losses obtained with the theoretical losses based on Faraday's laws (see fig. 20 (*b*) to 25 (*b*)) there are three conditions to be considered:

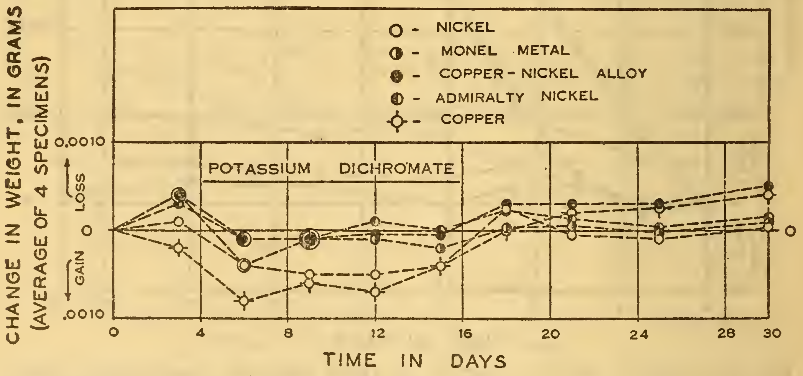


FIG. 18.—*Results showing progress of spray corrosion tests during 30-day period; N potassium dichromate solution (used as an oxidizing agent)*

(*a*) The actual loss is equal to the theoretical loss. This condition should be expected to obtain in cases where no effects are present to interfere with the uniform attack of the metal. The results with nickel in hydrochloric acid and sodium chloride and with copper in acetic acid (from 0.4 volt up), sodium chloride, and potassium dichromate serve admirably in confirming this expectation.

(*b*) The actual loss is less than the theoretical loss. This condition is to be interpreted as being the result of the formation of a more or less protective film which would tend to lessen the rate of corrosion.

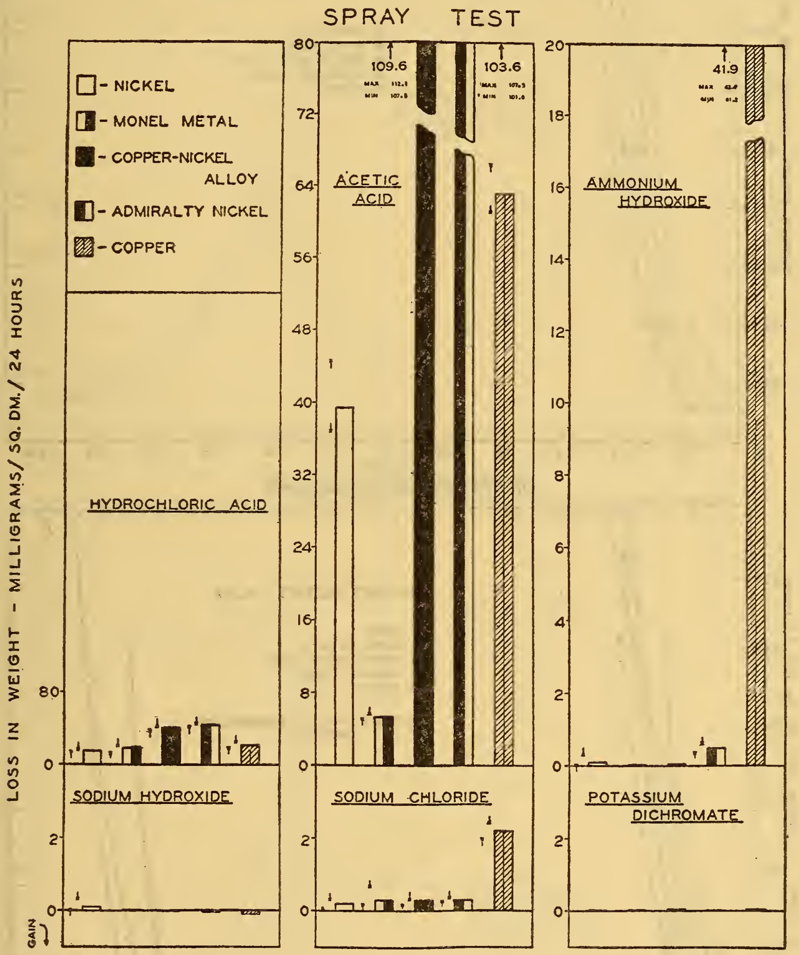


FIG. 19.—*Results of spray corrosion tests in N hydrochloric acid, acetic acid, ammonium hydroxide, sodium hydroxide, sodium chloride, and potassium dichromate solutions*

This film need not necessarily be a visible one; the existence of invisible oxide films on metals has been demonstrated in an interesting manner by Evans.[14] The results with nickel in acetic acid, sodium and ammonium hydroxides and potassium dichromate and by copper

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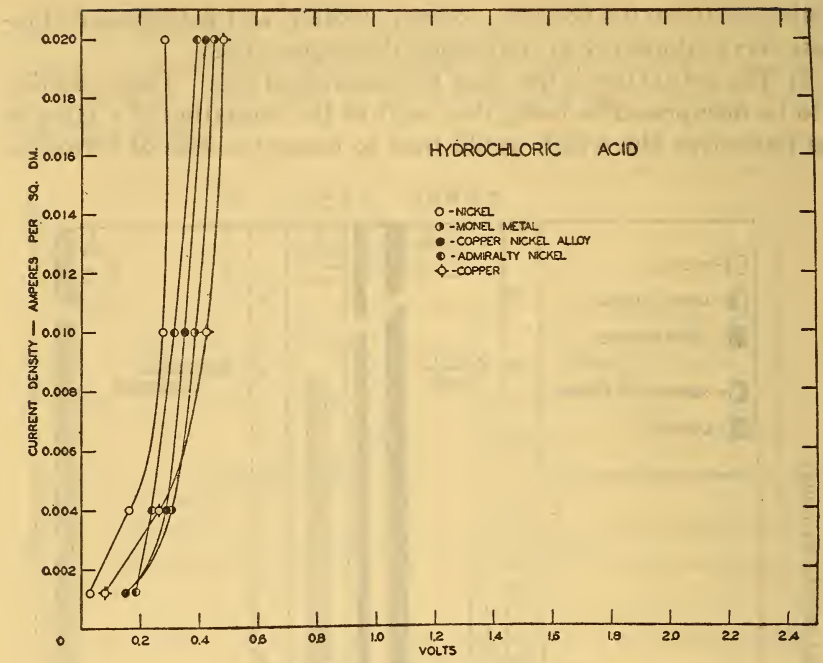
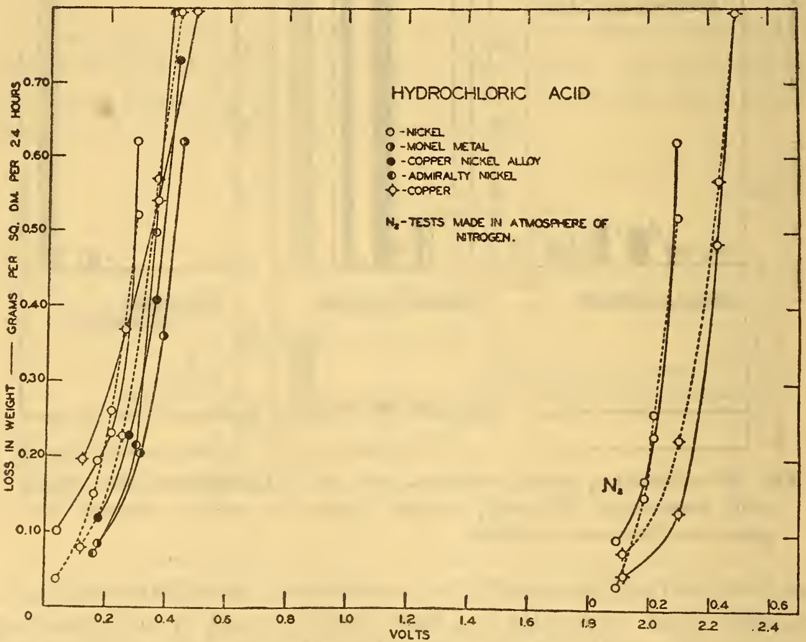
[14] U. R. Evans, "The passivity of metals. Part I. The isolation of the protective film," J. Chem. Soc., **131**, p. 1020; 1927.



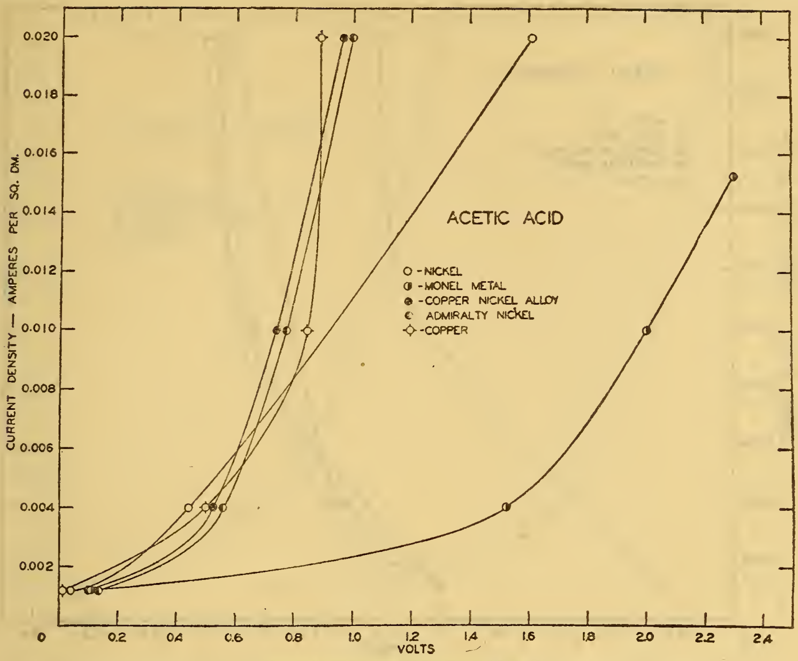
(a) *Current density-potential curves*



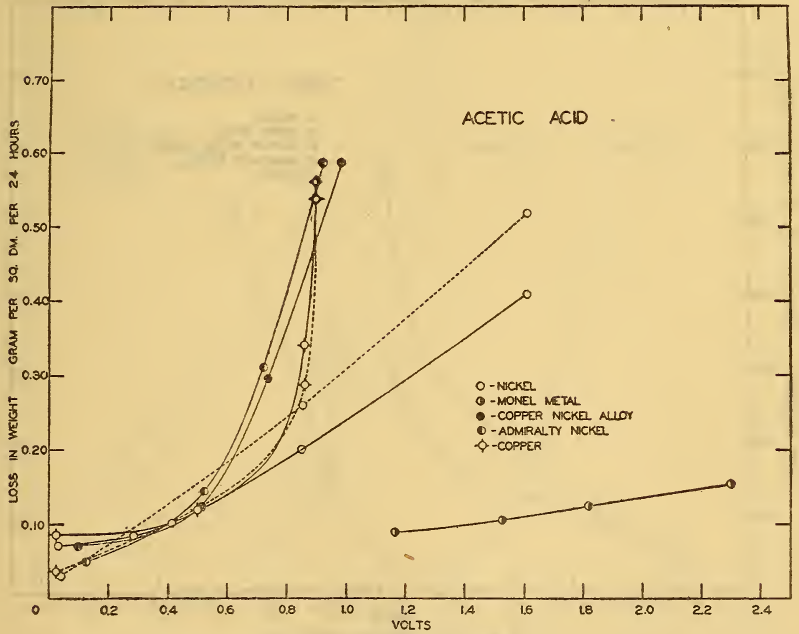
(b) *Loss in weight-potential curves*

Fig. 20.—*Results of accelerated electrolytic corrosion in N hydrochloric acid solution*

The dotted curves are the theoretical losses in weight (for nickel and copper as Cu$^{\bullet}$), which were computed on the basis of Faraday's laws for the current densities resulting from the potentials used



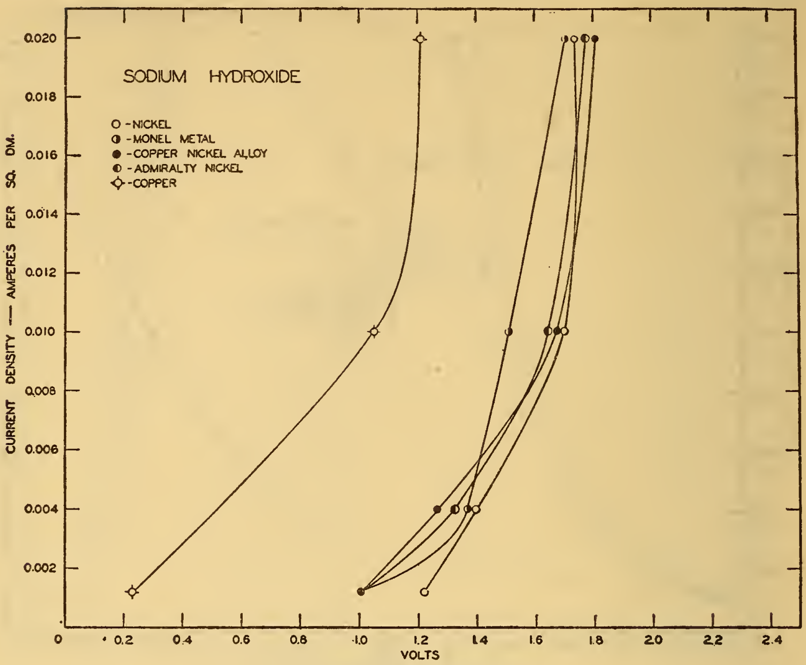
(a) *Current density-potential curves*



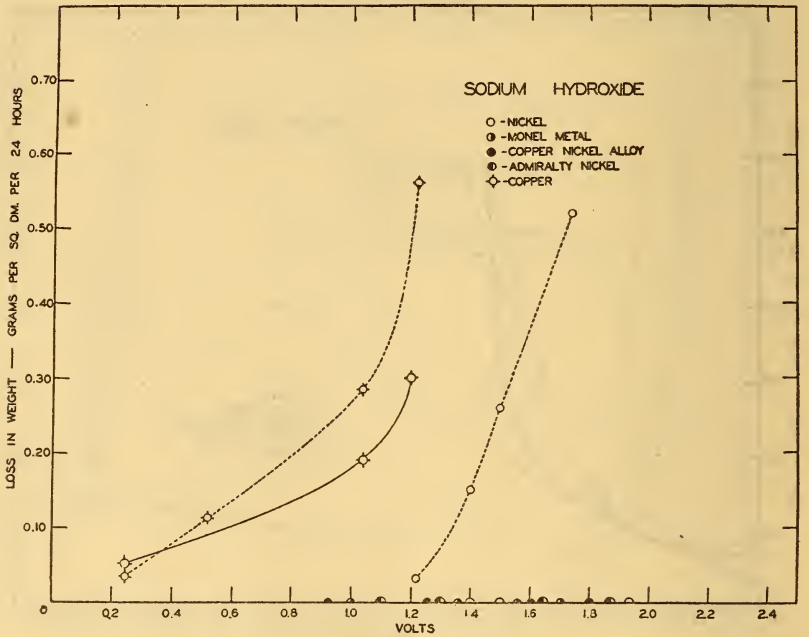
(b) *Loss in weight-potential curves*

FIG. 21.—*Results of accelerated electrolytic corrosion in N solution of acetic acid*

The dotted curves are the theoretical losses in weight (for nickel and copper as Cu•), which were computed on the basis of Faraday's laws for the current densities resulting from the potentials used



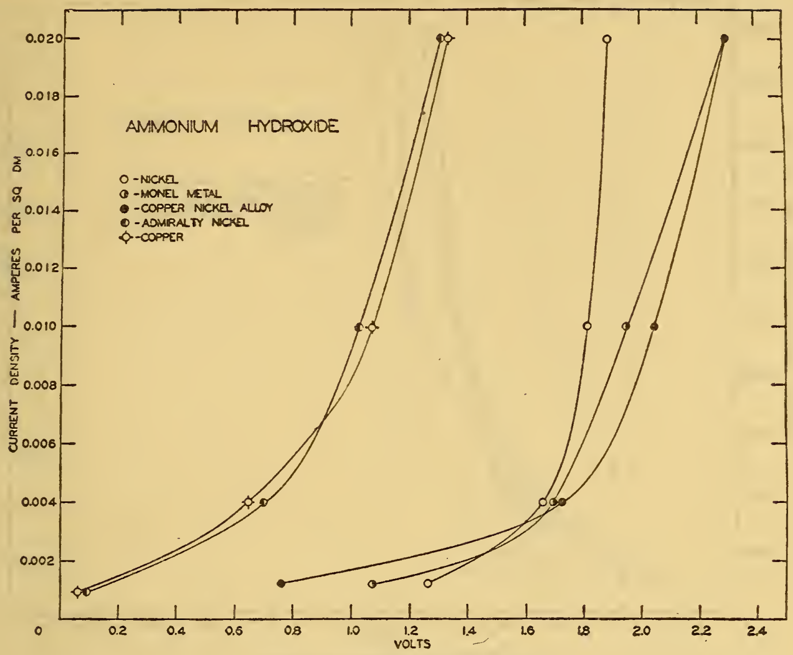
(*a*) *Current density-potential curves*



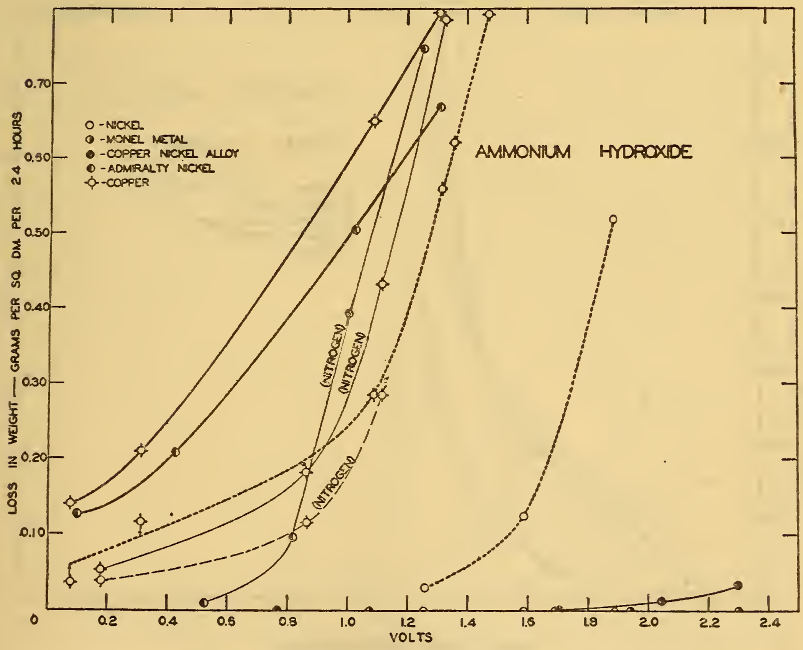
(*b*) *Loss in weight-potential curves*

FIG. 22.—*Results of accelerated electrolytic corrosion in N solution of sodium hydroxide*

The dotted curves are the theoretical losses in weight (for nickel and copper as Cu•), which were computed on the basis of Faraday's laws for the current densities resulting from the potentials used



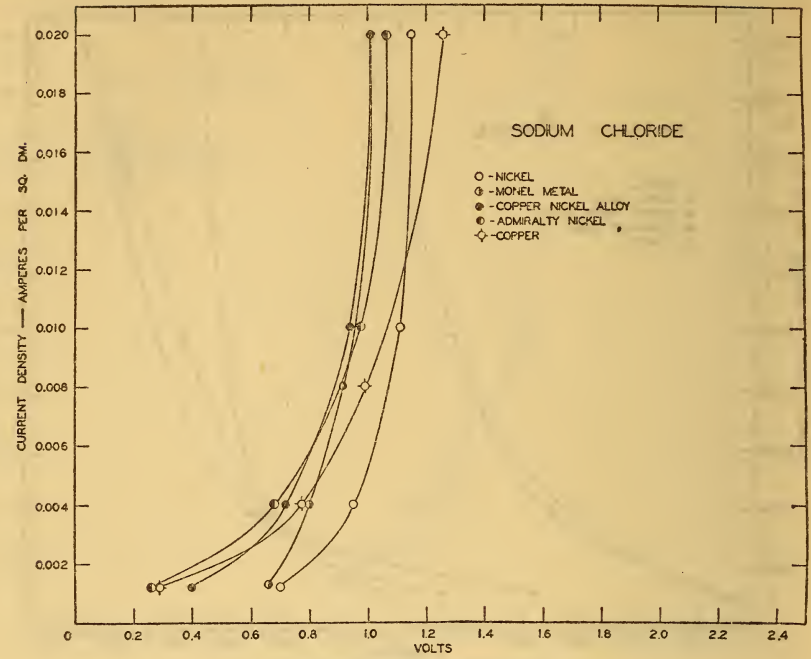
(*a*) *Current density-potential curves*



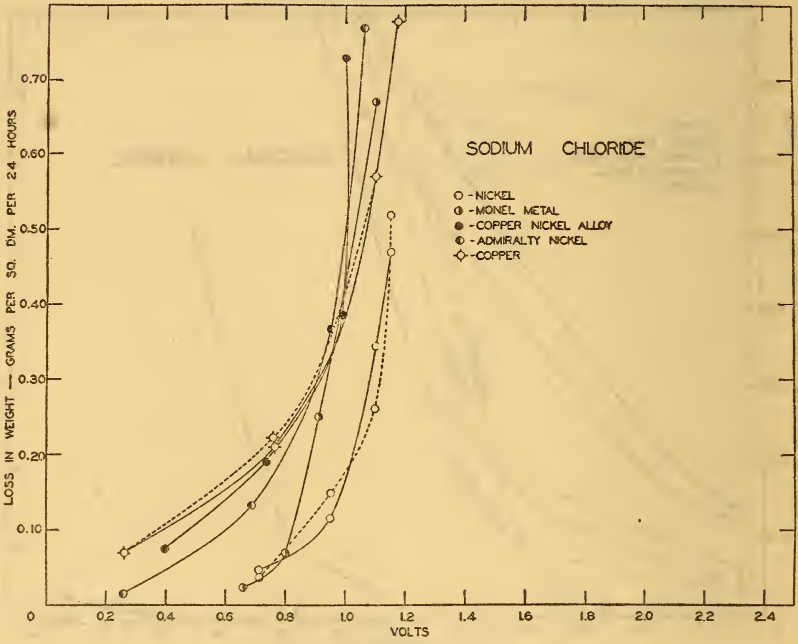
(*b*) *Loss in weight-potential curves*

FIG. 23.—*Results of accelerated electrolytic corrosion in N solution of ammonium hydroxide*

The dotted and dashed curves are the theoretical losses in weight (for nickel and copper as $Cu^{\bullet}$), which were computed on the basis of Faraday's laws for the current densities resulting from the potentials used



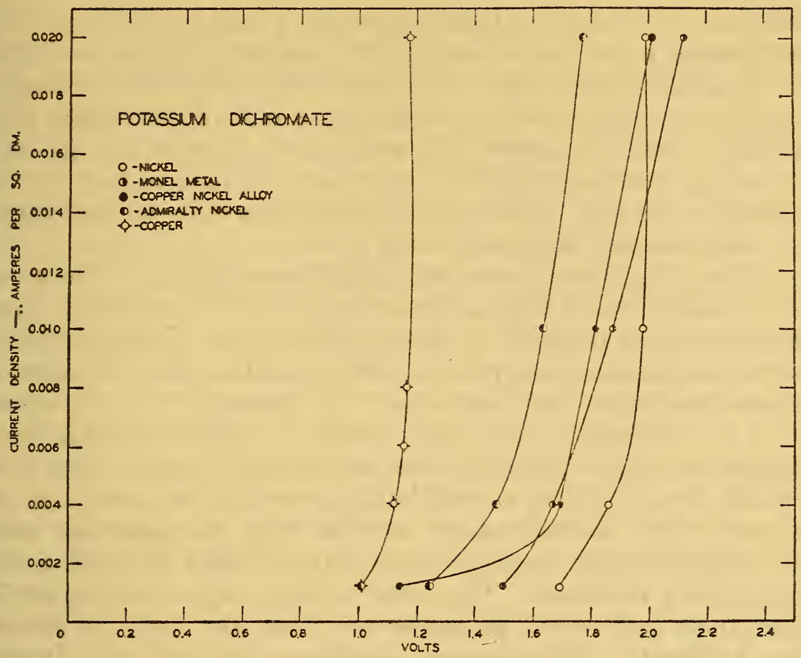
(a) *Current density-potential curves*



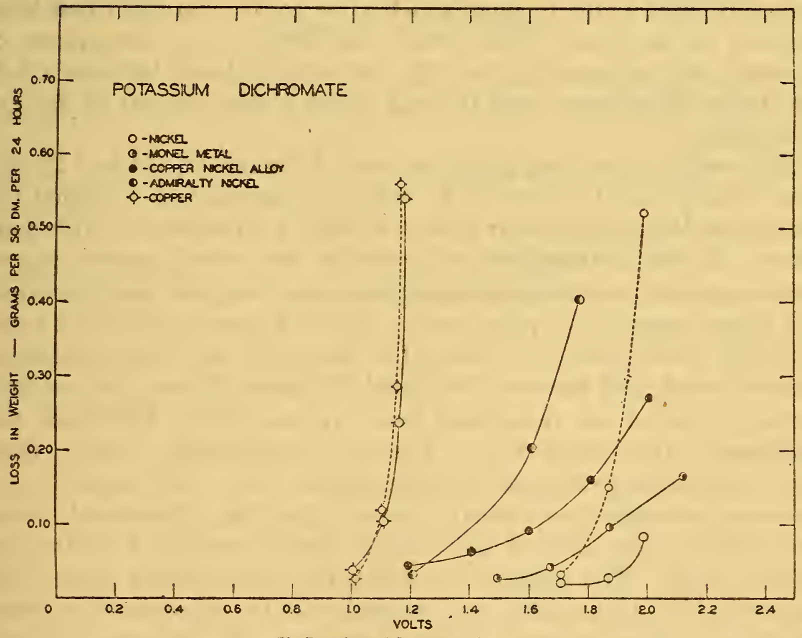
(b) *Loss in weight-potential curves*

FIG. 24.—*Results of accelerated electrolytic corrosion in N solution of sodium chloride*

The dotted curves are the theoretical losses in weight (for nickel and copper as $Cu^{\bullet}$), which were computed on the basis of Faraday's laws for the current densities resulting from the potentials used



(a) *Current density-potential curves*



(b) *Loss in weight-potential curves*

FIG. 25.—*Results of accelerated electrolytic corrosion in N solution of potassium dichromate*

The dotted curves are the theoretical losses in weight (for nickel and copper as Cu ●), which were computed on the basis of Faraday's laws for the current densities resulting from the potentials used in sodium hydroxide are in good agreement with this condition. The same tendency was also evinced by the nickel-rich alloys in sodium and ammonium hydroxides. It is to be expected that the corrosion of metals in chloride solutions would follow quite in accordance with Faraday's laws, by reason of the well-known action of chlorine ions in breaking down any protective film that may tend to form. This expectation has been well borne out in the cases of nickel and copper in sodium chloride, as already noted above.

(*c*) The actual loss is greater than the theoretical loss. The number of cases in which this condition holds true is very small. Consideration should be given, in accounting for them, to the possibility of certain conditions being present, such as aeration effects in solution, perhaps localized at the "water line," or "parasitic" e. m. f. effects caused by nonhomogeneity in the metal. In order to obtain some evidence as to the validity of these assumptions, several of the tests in which the actual loss exceeded the theoretical loss, computed on the basis of the current density resulting from the potentials used, were repeated under conditions such that the effect of aeration was reduced to a minimum. The tests included copper and nickel in hydrochloric acid as well as copper and Admiralty nickel in ammonium hydroxide. The solutions used were prepared from freshly boiled distilled water through which after cooling nitrogen had been bubbled for an hour. The "run" was made in an atmosphere of nitrogen, the polarization box (fig. 6) being inclosed beneath a bell jar filled with nitrogen, and through which a slow current of this gas was passed.

The results, which are given as part of Figures 20 (*b*) and 23 (*b*), show clearly that the amount by which the actual loss exceeded the theoretical loss in these four cases was largely an aeration (oxidation) effect. In the hydrochloric-acid solution the actual loss for copper when corroded in a nitrogen atmosphere was less than the theoretical loss (based upon the copper passing into the cuprous condition) and distinctly lower than that obtained in the earlier tests where nitrogen was not used, and the loss for nickel, except with very low-current density, equaled the theoretical loss. In ammonium hydroxide the decrease in the corrosion loss was very considerably greater than the corresponding decrease in hydrochloric acid. The actual losses, however, remained somewhat greater than the theoretical losses computed on the basis of the current density produced by the potentials used. The amount by which the actual losses exceed the theoretical in these cases are properly to be attributed to some other cause than aeration. The appearance of the surface of the copper and copper alloy specimens corroded with ammonium hydroxide was also somewhat different when the nitrogen atmosphere was used from that of specimens corroded in the ordinary manner.

When corroded in the nitrogen atmosphere the surface was slightly blackened only below the "water line," the portion above being clean and apparently unattacked, whereas when nitrogen was not used considerable surface blackening occurred above the "water line" in addition to the pronounced darkening below this line. The more detailed study of the subject which is soon to be undertaken may be expected to throw more light on these and other related points concerning the accelerated electrolytic corrosion test.

It should be noted, in passing, that the relative position of the theoretical loss curves for nickel and copper in hydrochloric acid is reversed from that for all the other solutions. It is interesting to note that this reversed relative position coincides with the relationship in which the losses in weight obtained for nickel and copper in nitrogen-saturated hydrochloric acid stand. (See fig. 12.)

It would seem from the results obtained with copper, nickel, and copper-nickel alloys that, speaking from a general standpoint, the greatest value to be derived from the accelerated electrolytic test lies in showing whether or not a metal will form a protective film under corrosive conditions. On the other hand, these results are not extensive enough to warrant a recommendation of the electrolytic test in place of the ordinary simple immersion as a laboratory testing method.

2. EFFECT OF AERATION

The fact is well established that the attack of a metal when immersed in a corrosive solution is decidedly dependent upon the degree of aeration of the solution used. [15, 16, 17, 18] Of the various factors affecting corrosion in a practical way, this one, without question, is of the most importance.

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[15] O. B. J. Fraser, D. E. Ackerman, and J. W. Sands, "Controllable variables in the quantitative study of the submerged corrosion of metals," Ind. Eng. Chem., **19**, p. 332; 1927.

[16] R. P. Russell and A. White, "Effect of oxygen concentration on the corrosion of copper by nonoxidizing acids," Ind. Eng. Chem., **19**, p. 116; 1927.

[17] J. F. Thompson and R. J. McKay, "The control of motion and aeration in corrosion tests," Ind. Eng. Chem., **15**, p. 1114; 1923.

[18] W. G. Whitman and R. P. Russell, "The acid corrosion of metals; effect of oxygen and velocity," Ind. Eng. Chem., **17**, p. 348; 1925.

TABLE 3.—*Accelerating effect of aeration in simple immersion and in repeated immersion, as expressed in per cent increase in the corrosion rate (loss in weight, mg/dm ^{2}/24 hours) over that obtained under less aerated conditions ("nonaerated" in simple immersion and "interruptedly immersed" in repeated immersion)*

	Simple immersion					
	HCl	HAc	NH_4OH	NaOH	NaCl	$K_2Cr_2O_7$
Nickel	206	213	0	−6	8	−24
Monel metal	1, 725	248	−33	16	−40	13
Copper-nickel alloy	2, 310	120	−60	4	26	0
Admiralty nickel	5, 686	307	23	32	81	−60
Copper	3, 105	442	191	98	662	144
	Repeated immersion					
	HCl	HAc	NH_4OH	NaOH	NaCl	$K_2Cr_2O_7$
Nickel	187	−11	67	0	340	−43
Monel metal	228	758	−46	−60	−20	77
Copper-nickel alloy	1, 450	262	29	0	125	−22
Admiralty nickel	826	1, 521	283	100	64	0
Copper	407	674	555	581	143	0

NOTE.—The values given here represent the ratio, $\frac{c}{b}\times 100$, where *c* is the difference (*a*—*b*) in loss in weight for the aerated (*a*) and nonaerated (*b*) specimens in simple immersion or for the continuously immersed (*a*) and interruptedly immersed (*b*) specimens in repeated immersion.

The results previously summarized show that the increase in the corrosive attack of any given solution resulting from aeration varies decidedly with the different metals. Of the five, copper was affected in the greatest degree. This is probably to be attributed to the decidedly greater solubility of the cupric salts as compared to the solubility of the cuprous salts. Table 3, in which the accelerating effect of aeration in simple immersion and repeated immersion is illustrated by numerical data, tends to bear this out. In some cases, as indicated in this table by a negative sign, the effect of aeration was apparently of a negative character; that is, the loss in weight of the specimens less exposed to oxidizing conditions was greater than that of those intentionally exposed to the accelerating effect of oxidizing conditions. Even in still solutions which were not intentionally aerated much of the corrosion should properly be attributed to aeration as was demonstrated by the results obtained by agitating the solution with nitrogen (fig. 12). These results also serve to show how the effect of aeration varies for different metals in the same solution. The decrease in the attack of nickel by hydrochloric acid produced when nitrogen was used for agitating the solution was almost insignificant as compared with the effect upon copper under these conditions. A still further decrease in the attack of copper was obtained, as indicated by the lower (dotted circle) of the two values for copper in Figure 12, in a special run wherein a quite vigorous bubbling of nitrogen gas into the corroding medium was maintained for 45 minutes before and 35 minutes after the specimens were placed in the test bottles with the object of driving out as much as practicable of the dissolved oxygen from the solution and of the oxygen from the atmosphere overlying the solution in the test bottles.

The increase in the corrosive attack resulting from repeated immersion as compared with the attack in simple immersion (unaerated) is logically to be attributed to aeration. The effect of continuous repeated immersion was, on the whole, considerably greater than that of intermittent repeated immersion. This may be attributed in part to the greater length of time the specimens were in contact with the solution in the former as compared with the latter. In the 15-minute cycle of the intermittent repeated-immersion tests the specimen was immersed, at least partially, in the solution for approximately 1½ minutes, whereas in the continuous repeated immersion tests for the same length of time the specimen was in contact with the solution for approximately five times as long. The results of corrosion by continuously repeated immersion, however, bear no consistent relation to those obtained by intermittently repeated immersion, which suggests that the difference in the length of time the specimens were immersed in the two cases was not the controlling factor. A variable of probably greater importance is the greater opportunity for differential aeration in continuously repeated immersion than in the other case. The work of Evans [19] has clearly shown that a difference in the degree of aeration of portions of a metal immersed in a solution is a decided accelerant of corrosion. In the "oxygen concentration" cell thus resulting, the part of the metal more strongly aerated acts cathodically with respect to the less fully aerated part. As a consequence, the latter, the anode of the cell, corrodes much more rapidly than would be the case if the specimen was immersed, but was not aerated.

In the repeated-immersion tests there would seem to be good opportunity for differential aeration, as the sample was partially immersed either on lowering or raising and also as the solution drained from the specimen when it was withdrawn from the solution. The total aggregate effect of such differential aeration would be very considerably less for specimens immersed only once every 15 minutes than for those immersed five times as frequently.

Another important factor affecting the corrosion rate was the tendency in several cases for the corrosion product to be retained on the surface of the metal as a film which afforded at least some degree of protection of the underlying metal from the attack of the solution. In intermittently repeated immersion this tendency, without doubt, was greater for any particular combination of metal and solution than for the same combination when corroded by continuously repeated immersion. Likewise, many of the low-corrosion rates can be attributed to this tendency toward film-formation, such as in the case of hydrochloric acid in which the corrosion product, the relatively insoluble cuprous chloride, formed a protecting film, whereas in acetic acid the greater solubility of the corrosion product was not conducive to the formation of such a film. In the case of sodium hydroxide, the film which formed on copper and the copper-rich alloys was great enough to be detected by the gain in weight of these specimens.

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[19] Evans, U. R., Corrosion of Metals, Edward Arnold & Co., London, 2d ed.; 1926.

3. THEORETICAL ASPECTS

Concerning the theoretical aspects of the corrosion of metallic solid solutions, Tammann[20] says:

> In homogeneous binary solid solutions subjected to a chemical reagent it will generally be found that the two components will be attacked unequally. In cases where the one component is practically unattacked, it will be found that the nobler component exerts a protective influence on the less noble component up to a certain limiting value.

The results of the present investigation, however, indicate that in applying this generalization to commercial alloys of the solid-solution type careful consideration must be given to the method by which the corrosive attack has been carried out. In a good many cases the corrosion rates for the three alloys were found to lie between that for nickel, which for most of the tests was by far the more resistant of the two metals, and that for copper. The "protective action" of the more noble component upon the solid solutions is strikingly illustrated by the results obtained with ammonium hydroxide and in a somewhat less pronounced way by the tests with sodium hydroxide. These results (figs. 9, 10, and 22 (*b*)) show that an alloy containing as much as 70 per cent of copper may have a very high degree of resistance against a solution which corrodes copper at a very rapid rate. Another illustration of the "protective action" of the nobler component may, in a general way, be found in Table 3.

The other test results, however, show that the corrosion conditions often play a very important rôle in determining the relative corrodibility of a series of alloys and metals, as is illustrated by the results obtained with hydrochloric acid (figs. 7 and 19). Under some conditions the relative resistance of the two metals, copper and nickel, toward the same solution may be reversed, as is shown by the repeated immersion tests in acetic acid (fig. 8). The most consistent agreement with Tammann's generalization was obtained in the simple immersion tests in still (unaerated) solutions, in the interrupted repeated immersion tests, and in some of the accelerated electrolytic tests; for example, Figure 25. In many of these, however, the corrosion rate for at least some of the alloys was found to be less than that of the more noble component, nickel, and even in the tests in which oxidation was reduced to a minimum by the use of nitrogen (fig. 12) this tendency was pronounced.

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[20] Tammann, Gustav, A Text Book of Metallography; translation by R. S. Dean and L. G. Swenson, Chemical Catalog Co., publishers, p. 305; 1925.

In brief, the results of the tests in this investigation indicate that for commercial copper-nickel alloys of the solid solution type the degree of the ennobling effect of nickel varies not only with the corrosive solution but with other conditions which obtain during the progress of corrosion, particularly the aeration factor, and also the nature of the protective film that may be formed.

VII. SUMMARY

1. The corrosion resistance of five members of the copper-nickel alloy series, ranging from commercial copper to commercial nickel and including three commercial copper-nickel alloys, all in sheet form, was determined in six solutions—hydrochloric acid, acetic acid, sodium hydroxide, ammonium hydroxide, sodium chloride, and potassium dichromate.

2. The corrosive solution was applied to the metal in several ways so as to permit a wide range in the possible effect of aeration and film formation. The testing methods included simple immersion in unaerated and in aerated solutions, repeated immersion, both continuous and intermittent, exposure in an inclosed space to a "spray" or mist of the corrosive solution, and accelerated electrolytic corrosion at low-current densities. A few tests in which nitrogen was used instead of air for agitating the solution supplemented the ordinary simple immersion tests.

3. The corrosion rate and the order of relative corrodibility of the five materials were found to vary very considerably for the different test methods, thus showing that a corrosion test designed to give information concerning the suitability of a metal for some particular type of service should embody the essential features of the service which is to be met.

4. The agreement of the results of accelerated electrolytic corrosion tests (at very low-current densities) with those of simple immersion was, on the whole, somewhat better than the agreement of the results of the other types of test used with those of the simple immersion method. The data are not extensive enough, however, to warrant any recommendation concerning the use of the electrolytic test in preference to the other.

5. The degree of aeration of the corroding solution is one of the most important factors which control the rate of corrosion of a metal under varying conditions. The results obtained with solution deaerated by means of nitrogen showed that the aeration effect in

laboratory corrosion tests may be very considerable even when the solution is not intentionally aerated.

6. The tendency of the corrosion product to form a relatively insoluble, impervious surface film whereby, after the initial attack, the underlying metal is protected against any pronounced continued corrosive attack by the solution is in many cases the controlling factor which determines the corrosion rate. In many instances in the spray tests this effect was so marked that the corrosion rate was very decidedly less than that of the same metals when corroded by the same solutions by immersion methods.

7. The results confirm, in a general way, Tammann's generalization concerning the corrodibility of binary metallic solid solutions, which is to the effect that the rate of chemical attack of two metals in the form of a solid solution is different from that of either of the two metals alone and intermediate between them. The more noble component serves to protect the more reactive one up to a certain limiting value. Striking evidence of this was obtained in the case of ammonium hydroxide, which attacks copper very severely but had an enormously less effect upon the nickel-copper solid solutions even upon that of relatively high copper content. In many of the tests with various solutions the corrosion rate of some of the solid solutions was less that that of the more noble component. The results of the tests in which the accelerating effect of aeration was reduced to a minimum by bubbling nitrogen through the solution also served to confirm this.

WASHINGTON, November 26, 1927.

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